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EGE UNIVERSITY
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TREATMENT OF LIGNOCELLULOSIC BIOMASS BY CO-SOLVENT FOR HIGH YIELD OF SACCHARIFICATION: INVESTIGATION OF STRUCTURAL CHANGES IN BIOMASS USING FTIR ANALYSIS

MSc Thesis

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Sanaz SAMADI ZENOUZ tarafından yüksek lisans tezi olarak sunulan "Yüksek oranda şeker verimi için lignoselülozik biyokütlenin yardımcı çözücü ile işlemden geçirilmesi: FTIR analizi ile biyokütledeki yapısal değişikliklerin araştırılması" başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve ..... tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ETİK KURALLARA UYGUNLUK BEYANI

E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "Yüksek oranda şeker verimi için lignoselülozik biyokütlenin yardımcı çözücü ile işlemden geçirilmesi: FTIR analizi ile biyokütledeki yapısal değişikliklerin araştırılması (Treatment of lignocellulosic biomass by co-solvent for high yield of saccharification: Investigation of structural changes in biomass using FTIR analysis)" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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İmzası

Adı-Soyadı

Sanaz SAMADI ZENOUZ

ÖZET

YÜKSEK ORANDA ŞEKER VERİMİ İÇİN LİGNOSELÜLOZİK BİYOKÜTLENİN YARDIMCI ÇÖZÜCÜ İLE IŞLEMDEN GEÇİRİLMESİ: FTIR ANALİZİ İLE BİYOKÜTLEDEKİ YAPISAL DEĞİŞİKLİKLERİN ARAŞTIRILMASI

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Petrol kaynaklaının sınırlı olması ve sera gazı emisyonlarıyla ilgili artan endişeler, alternatif enerji kaynaklarına yönelik araştırmaları artmıştır. Lignoselülozik biyokütle, biyoyakıt ve biyokimyasal üretim için en yüksek potansiyel hacme ve en düşük maliyete sahip olması nedeniyle alternatif enerji için ana seçimdir.

Bu projede, lignoselülozik biyokütlede yüksek oranda şeker verimi ve yapısal değişiklikler için yardımcı çözücü işleminin etkileri araştırılmıştır. Badem kabukları gerçek bir biyokütle olarak kullanılmıştır. Deneysel çalışmalarda kullanılan badem kabuklarının selüloz, hemiselüloz ve lignin içeriğini belirlemek için Van Soest analizi yapılmıştır.

Badem kabuğunun farklı çözücüler ve yardımcı çözücüler (su, etil asetat, aseton ve asetonitril suda 1: 1 oranında) kullanılarak kimyasal ön işlemle şekerleşmesi otoklav reaktörlerinde gerçekleştirilmiştir. Sıcaklık ve katı/çözücü oranı gibi reaksiyon koşulları sırasıyla 180 °C'de ve 2 g katı/18 mL çözücüde sabit tutuldu. Deneyler 20, 40 ve 60 dakika süreler için gerçekleştirilmiştir.

Hem biyokütle numunesi hem de işlem sonrası katı bakiye FTIR analizi ile değerlendirilip ve lignin, hemi-selüloz ve selülozun yapısal ayrışması araştırılmıştır. Bunun yanı sıra çalışmamızın temelini teşkil eden şekerleşme ve oluşan şeker türleri ile oluşacak organik asitler için sıvı ürünün HPLC analizine tabi tutulmuştur. Ayrıca sıvı ve katı için TOC analizleri yapılmıştır. Bu sayede farklı çözücülerin yapısal etkileri değerlendirilmiştir.

Anahtar sözcükler: Biyokütle, Badem Kabuğu, Şekerleşme, yardımcı çözücü

ABSTRACT

TREATMENT OF LIGNOCELLULOSIC BIOMASS BY CO-SOLVENT FOR HIGH YIELD OF SACCHARIFICATION: INVESTIGATION OF STRUCTURAL CHANGES IN BIOMASS USING FTIR ANALYSIS

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Potential petroleum energy limitations and rising concerns about greenhouse gas emissions are driving up interest in research into alternate energy sources. Lignocellulosic biomass is a main choice for alternative energy since it has the highest potential volume and lowest cost for biofuel and biochemical production.

In this project, the effects of co-solvent treatment for high saccharification yield and structural changes in lignocellulosic biomass were investigated. Almond shells were selected as a real biomass feedstock. A Van Soest analysis was performed on almond shells that were used in experimental studies to determine their cellulose, hemicellulose, and lignin content.

The saccharification of almond shell by chemical pre-treatment using different solvents and co-solvents (water, ethyl acetate, acetone, and acetonitrile in water at a ratio of 1: 1) was carried out in the autoclave reactors. Reaction conditions such as temperature and solid/solvent ratio were held constant at 180 °C and 2 g solid/18 mL of solvent, respectively. The experiments were performed for 20, 40, and 60 minutes.

Both the biomass sample and the post-treatment solid residue were evaluated by FTIR analysis, and the amount of breakdown of lignin, hemi-cellulose, and cellulose was investigated. In addition, the liquid product was subjected to HPLC analysis for the saccharification and sugar types that are the basis of our study and the organic acids that formed in the experiments. TOC analyses were carried out for liquids and solids. In this way, the structural effects of different solvents were evaluated.

Key Words: Biomass, Almond Shell, Saccharification, Co-Solvent

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LIST OF SYMBOLS AND ABBREVATIONS

Symbols	Explanations
T	Temperature
P	Pressure

Abbreviations

g	gram
mg	milligram
wt	weight
min	minute
h	hour
L	Liter
mL	milliliter
mM	millimolar
EJ	Exajoule
TOC	Total Organic Carbon
TC	Total Carbon
IC	Inorganic Carbon
HPLC	High Performance Liquid Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
SSM	Solid Sample Module
CLE	Carbon Liquefaction Efficiency

1. INTRODUCTION

Energy is an important topic for the socioeconomic development of every nation, and as a result of quickening industrialization and population growth, energy requirements across the world are continuously growing. As stated by the Energy Global Status Report (GSR), the great bulk, or 78.4%, of the energy needs of the globe are addressed by nonrenewable fossil fuels, such as natural gas, coal, and oil, while renewable resources like solar, hydropower, wind, and biomass account for just 19 percent (Dwyer and Teske, 2018).

Nonrenewable fossil fuel stocks are limited and fast dwindling due to growing demand, limiting their future utility in meeting the world's energy demands. Furthermore, rising levels of air pollutants (i.e., CO, SOx, and NOx) generated by fossil fuel burning have motivated researchers to explore more sustainable and eco-friendly alternative energy sources. In this sense, biomass is a crucial supply for achieving the goal.

The term "biomass" includes all organic substances present in the biosphere, making it the sole renewable energy source that contains carbon (Perea-Moreno et al., 2019).

Lignocellulosic biomass (LCB), one of the viable long-term sources of energy and chemicals, can be derived from plant growth and can come from plantations, natural regrowth woods, and annual field crops, or remnants of any of the aforementioned (Nunes et al., 2020). It is composed mostly of three organic elements known as cellulose, hemicellulose, and lignin. Considering the kind of biomass, plant species, and even the origin of the biomass, these polymers are linked together in a heteromatrix to varying degrees and have distinct compositions. In trace proportions, lignocellulosic biomass also contains oils, inorganic compounds, proteins, and extractives, albeit none of these ingredients have a notable impact on the material's structure (Pasangulapati et al., 2012).

To generate energy and extract platform chemicals, lignocellulosic biomass must first be pre-treated. Overcoming lignocellulosic biomass's recalcitrance is important in this procedure. The reason for the recalcitrance is the cellulose's

highly crystalline structure, which is enclosed in a lignin and hemicellulose-based polymer matrix.

Cellulose is an insoluble state in water. Based on the literature, cellulose's poor water solubility is caused mostly by hydrophobic interactions in cellulose's crystal structure. According to the cellulose structural analysis, ribbons generated by side-by-side hydrogen bonds yield distinct polarities in molecules. In an aquatic environment, the hydrophilic sides have a propensity to cling to one another, resulting in the material's poor solubility in water. To tackle this issue, more effective solvents with amphiphilic properties should be utilized, such as substances having polar and nonpolar portions and highly polarisable ionic groups in their structures. This issue can also be solved with co-solvents. Along these lines, urea, polyethylene glycol, glycerol, alcohols, and acetone in water may be interesting compounds that help cellulose dissolve in water (Dilip and Chakraborty, 2019; Kalashnikova et al., 2012).

The four categories of physicochemical, physical, chemical, and biological pretreatment techniques are the most prevalent subcategories, the effects of which change depending on the approach employed, the kind of biomass utilized, and the process parameters used.

Chemical pretreatments of lignocellulosic biomass include diluted acid, lime, ionic liquids, and co-solvent application.

Cellulose is a highly polymerized glucose polymer composed of 10,000 glucose reparative units connected together by 1,4 glycosidic units. Biomass depolymerization is a mass-and heat-transfer process because of the potent inter- and intramolecular hydrogen interactions in the lignocellulosic structure, and one of the probable methods for cellulose depolymerization is the pre-treatment of lignocellulosic material.

Solvent handling allows for cellulose depolymerisation. The polarity, dielectric constant, and solubility specifications of the solvent all affect its efficiency. One of the essential prerequisites for a high level of polymer solubility

within these parameters is the solubility parameter. To achieve excellent dissolving, the cellulose polymer's and solvent's solubility parameters ought to be as near to identical as possible (Bhatia et al., 2020).

In this research, enhanced saccharification of almond shell by chemical pre-treatment using different solvents and co-solvents like water and a mixture of water-ethyl acetate, water-acetone, and water-acetonitrile has been looked into. Reaction parameters like temperature and solid/solvent ratio were maintained constant since they have already been confirmed for maximum liquefaction of biomass in previous studies. The amount of breakdown of lignin, hemi-cellulose, and cellulose was appraised via the use of Fourier Transform Infrared Spectroscopy (FTIR). The distinctive wave numbers in order to decompose lignin and cellulose were monitored based on corresponding values. Besides the given values for FTIR spectra, the entire FTIR band for every single sample was interpreted to explain the dissolution effects of solvent and co-solvent systems.

In addition, the liquid product underwent HPLC analysis for the saccharification and sugar types and the organic acids produced throughout the tests. In addition, TOC analyses were performed for liquids and solids. In this manner, the structural impacts of various solvents were evaluated.

2. GENERAL INFORMATION

2.1 Worldwide Overview of Energy and Biomass Energy

Energy is a vital aspect that propels any country's socioeconomic progress.

Energy demand has been continuously climbing ever since the industrial age, and this increase is due to two factors:

a) The expanding human population.
b) The rise in energy consumption per person when rural, less wealthy cultures give way to industrial, wealthier ones.

In general, a civilization uses more energy per person the wealthier it is. The overall national energy needs must be satisfied by the world's energy supply. Because natural rules state that energy is uncreatable and unstoppable, all energy used must be derived from energy sources found in nature. These are the natural sources of energy:

1. Fossil fuels, including coal, in all its forms, crude oil, and natural gas
2. Nuclear fuels like thorium and uranium.
3. Renewable energy supplies include hydroelectric, geothermal, biomass, wind, and solar energy.

Two of the earliest forms of energy are, in essence, minerals that were created many millennia ago. The mechanisms involved in their development take a very long time (geological periods). These minerals will eventually run out since it's unlikely that they will be replenished naturally in the years ahead.

The third component falls under the heading of renewable, endlessly reproducible energy sources. It seems like common sense to think that these sources of energy will keep on providing humankind with energy in the immediate and distant future (Michaelides, 2012).

Non-renewable fossil fuels supply the great majority of the world's energy demands, based on the Energy Global Status Report (GSR) (Dwyer and Teske, 2018). But there is a scarce quantity of these materials available, and they will eventually run out if mining continues. In addition, air pollutants (for example, CO, SOx, and NOx) from combustion result in global warming, which causes scientists to explore alternative renewable energy sources (Kumar et al., 2020).

The energy sources' total ultimate gross energy consumption in 2017 rose by 2% versus the previous year to 370 EJ. Oil and petroleum-derived goods constitute 40% of all energy used globally, while coal and gas each account for 20% of this total. 80% of the energy utilized globally in 2017 came from fossil fuels as a whole.

Globally, renewable energy's proportion of the entire ultimate energy usage fell by 0.2 percent in 2017 to 17.7 percent in 2017 from 16.1 percent in 2016. Utilizing renewable energy has shown promise in meeting the world's energy requirements. The utilization of energy worldwide from 2000 to 2017 is displayed in the following table, split down by source:

Table 2.1.1 Gross final energy consumption globally (IEA, 2019).

	Total	Coal	Oil	Natural Gas	Nuclear	Renewables	Renewables (%)
2000	269	43.1	115	55.7	7.64	47.4	17.6%
2005	304	58.9	125	61.2	8.22	50.6	16.6%
2010	338	72.6	129	70.0	8.25	57.0	16.9%
2015	359	76.6	138	73.7	7.72	63.3	17.6%
2016	364	74.8	140	75.7	7.83	65.1	17.9%
2017	370	75.2	143	77.9	7.93	65.7	17.7%

Bioenergy (energy produced from biological resources) is the type of renewable energy that is most often utilized. In 2017, bioenergy contributed over 70% of renewable energy use.

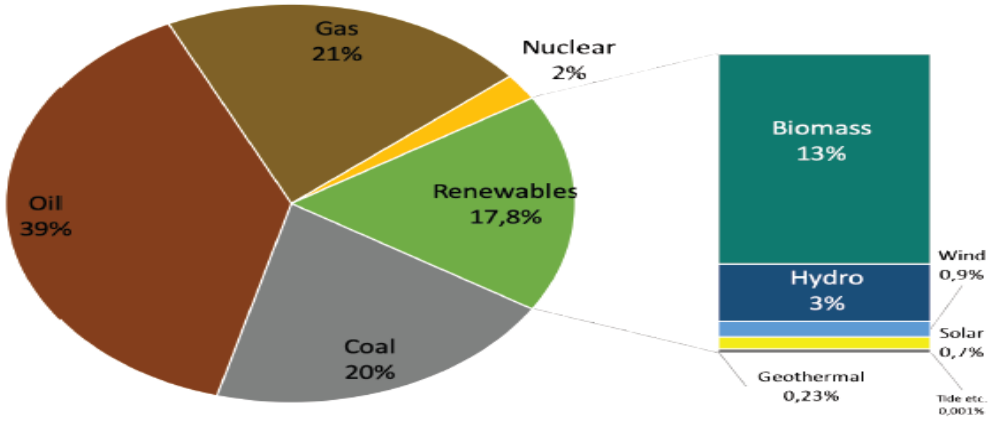

Figure 2.1.1 Gross final energy consumption in 2017 (IEA, 2019).

Municipal and industrial waste, primary solid biofuels, biogas, and liquid biofuels are typical categories for biomass sources. 2017 saw the usage of 55.6 EJ of biomass for energy, with major solid biofuels consisting of wood chips, wood pellets, and fuelwood for cooking and heating contributing to approximately 86% of that consumption. Liquid biofuels contributed to 7% of biomass. Biogas, municipal garbage, and industrial waste each contributed 2 to 3 percent (statistics, 2019).

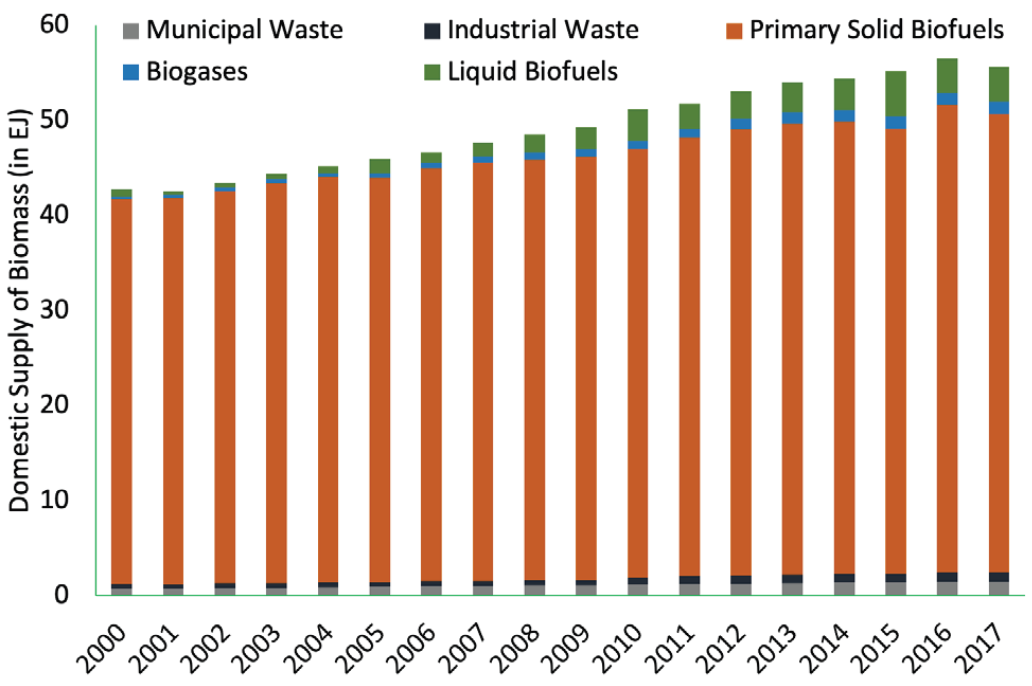

Figure 2.1.2 Domestic supply of biomass globally (IEA, 2019).

2.2 Biomass as Renewable Energy Resource

Biomass is gainfully employed to fulfill a diverse range of energy needs, including producing electricity, heating homes, fueling automobiles, and supplying process heat for industrial enterprises (Demirbaş, 2001).

As a source of clean renewable energy, biomass is among the most effective for attaining sustainable development because of its economic and social beneficial effects (Güney and kantar, 2020).

All organic material created by photosynthesis that exists on the earth's surface is referred to as biomass. All aquatic and terrestrial plants and trees, as well as waste biomass such as animal wastes, forestry and agricultural wastes, some types of industrial waste, municipal solid waste (MSW), municipal biosolids (sewage), and so forth, are all included.

In plants, chlorophyll uses photosynthesis to save solar energy as carbohydrates that, when burned, discharge their accumulated energy both as CO2 and water. In light of this, biomass functions as a natural battery, storing solar energy.

Figure 2.2.1 depicts a biomass energy cycle and how biomass is utilized to produce energy in an ecologically acceptable manner (Sriram and Shahidehpour, 2005).

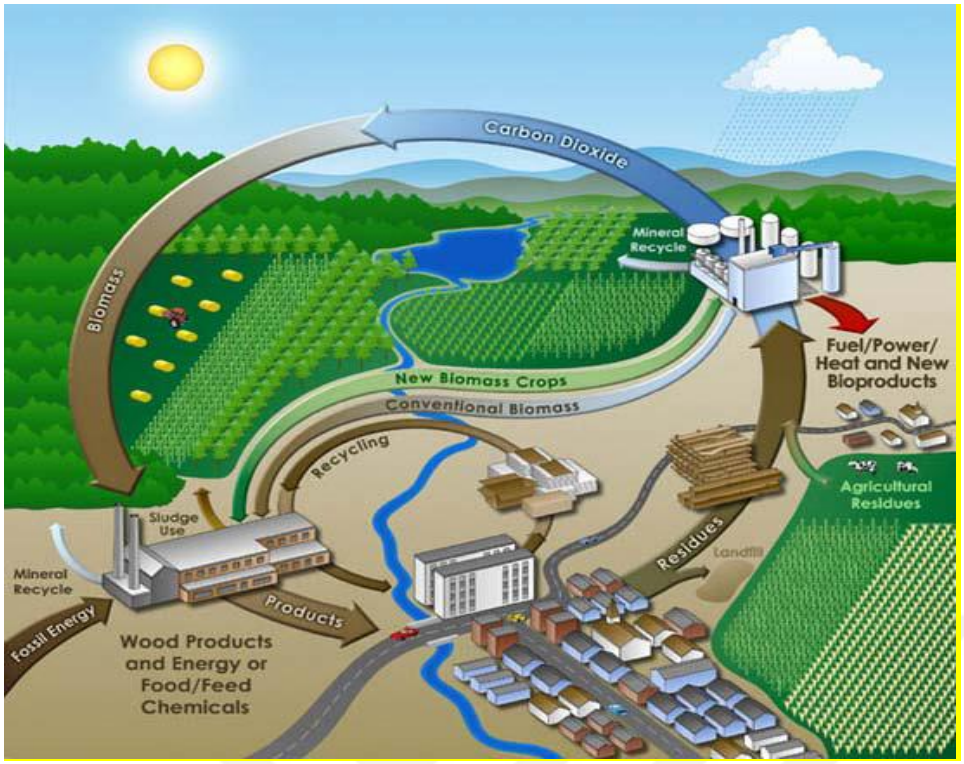

Figure 2.2.1 Biomass Energy Cycle (Sriram and Shahidehpour, 2005)

Numerous different energy carriers can be created from biomass through various treatment and conversion procedures. The sustainable end-product required, the nature and total volume of biomass, and the process cost are simply just some of the factors that go into determining which manufacturing method to use. There are three broad kinds of biomass accessible for energy production:

1. wastes
2. standing forests
3. energy crops

According to a nationwide study, the overall amount of biomass that may be gathered for energy generation varies greatly by industry. In line with national statistics from 2013, forestry contributes the most (about 88%), while crop leftovers produce just approximately 9% (Dalena et al., 2017).

Biomass energy falls into two kinds: modern biomass and traditional biomass. Biomass generated in a sustainable manner is referred to as "modern biomass," and it often includes large-scale applications and aspires to replace

traditional energy sources. Modern biomass encompasses the creation of power and heat, as well as fuel for vehicles, from agricultural and forest wastes and solid waste. In contrast, traditional biomass production is not sustainable and is mainly limited to underdeveloped nations and small-scale applications. It consists of household fuelwood and charcoal, rice husks and other plant remnants, and animal wastes (Goldemberg and Coelho, 2004).

The following are some advantages of utilizing biomass as a form of energy:

1. Biomass energy is a plentiful, reliable, environmentally beneficial, and renewable energy source. Since biomass collects the same quantity of carbon dioxide during growing just as it does when burned, it does not discharge CO_2 into the atmosphere.
2. The ability to produce energy from biomass using the same machinery or power plants that now burn fossil fuels is certainly one of the major strengths of employing this fuel.
3. There are no environmental consequences connected with biomass energy, such as acid rain, oil spills, radioactive waste disposal, open pits, river damming, or mining waste.
4. Biomass fuels are long-term. Biomass fuels come from green plants that fix carbon dioxide as they develop, therefore using them does not raise atmospheric carbon levels. Additionally, burning trash as fuel prevents the usage of polluting landfills.
5. Biomass-derived alcohols and other fuels are efficient, viable, and reasonably clean-burning.
6. Biomass is readily accessible and comparatively simple to grow throughout the entire planet (Sriram and Shahidehpour, 2005).

2.3 Turkey's potential for biomass

In Turkey, renewable energy sources constitute the second-largest energy-producing source after coal, and biomass supplies a considerable percentage of renewable energy generation.

Figure 2.3.1 depicts Turkey's existing and projected biomass energy production. By 2030, global biomass energy output is estimated to reach 52.5 Mtoe.

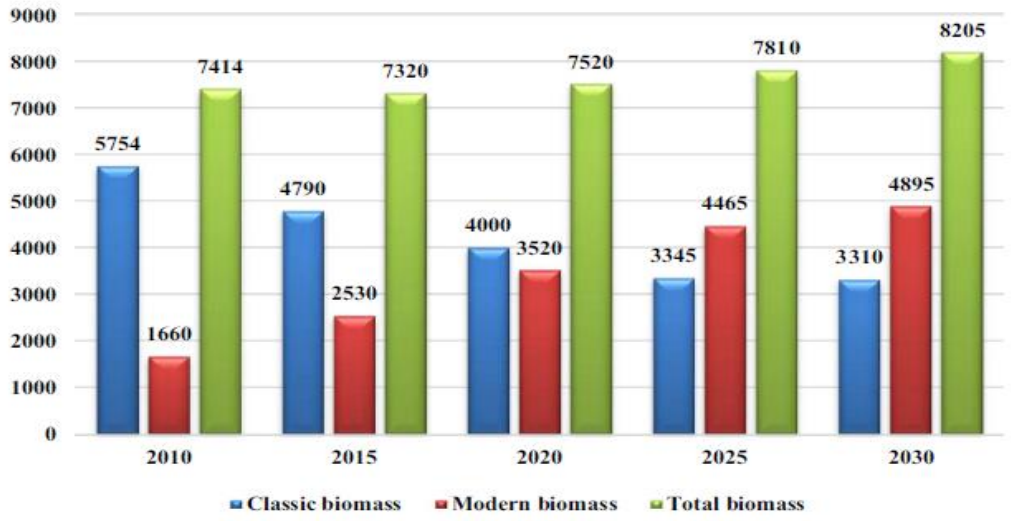

Figure 2.3.1 Turkey's current and future plans for biomass energy generation (Ktoe) (Ozturk et al., 2017).

✓ **Agricultural wastes**

Agricultural wastes are byproducts of the production and processing of non-valuable agricultural goods. About 90% of Turkey's agricultural output consists of crops and livestock. Cereal production accounts for around 75% of Turkey's cropland. Turkey has a huge agricultural potential, but very little waste is actually exploited. Given that 80% of grains may be used at a humidity rate of 15%, the total amount of agricultural wastes utilized in power plants would be between 27 and 36 million tons on average. The amounts of agricultural residues available in Turkey, as well as the biomass energy mix, are shown in Table 2.3.1.

Table 2.3. Evaluation of Turkish plant-based biomass sources (Ozturk et al., 2017).

Product	**Annual production (tons)**	**Energy content (MJ/kg)**
Wheat residues	30,000 – 40,000	18,40
Barley residues	12,000 – 16,000	17,10
Oats residues	400 – 600	17,70
Rye residues	350 – 450	17,60
Rice residues	250 – 350	15,40
Maize residues	4000 – 5000	16,80
Sunflower residues	2500 – 3000	14,28
Cotton seed residues	2600 – 3100	17,07
Sugar beet residues	1500 – 2000	16,72
Hazelnut shell	350,000	1.9 kWh
Walnut shell	150,000	20.18
Olive waste	450,000 t/1 million tons	12.5 – 21.0
Cocoon shell	1,000,000	5.3 kWh
Wood and woody Materials	12,000,000	62.3 kWh

✓ **Forest sources**

More than 25% of Turkey's entire land area is covered by forests (over 20 million hectares), with around half of that thought to be productive. Conifers (approximately 55 percent) and broad-leaved trees are the most prevalent kind of trees (more than 45%). With a yearly growth rate of roughly 25 million m3, the overall forest potential is approximately 935 million m3. The entire amount of timber generated in Turkish woods is anticipated to exceed 30 million m^3, with roughly 60% of that being used as firewood. Extremely productive woods account for around 90% of new growth. According to projections, 5 million hectares of fertile forestland are accessible for energy production. Table 2.3.2 illustrates Turkey's overall forest potential.

Table 2.3.2 Turkey's forest potential (Ozturk et al., 2017).

Forest potential	Resources (thousand m^3)	Annual growth (thousand m^3)
High productive (total)	847,032	25,605
Forest	88,30	4813
Other woodlands	758,732	20,792
Low productive (total)	88,479	2459
Forets	34,129	1115
Other woodlands	54,35	1344
Total	**935,511**	**28,064**

✓ Animal-based biomass

Every year, Turkey generates a large volume of animal waste. Most research on animal-based biomass has been conducted as part of biogas investigations. and development initiatives since the 1960s. Aside from feasibility studies on biogas consumption, a number of digesters have been built around the country. Table 2.3.3 shows representative animal-based residues and their overall energy potential (Ozturk et al., 2017).

Table 2.3.3 Turkey's whole and recoverable animal waste bioenergy potential (Ozturk et al., 2017).

Kind of animal	Total number of animals (thousand head)	Coefficient of conversion (ktoe per thousand animals)	Total energy potential (ktoe)	Recoverable energy potential (ktoe)
Sheep and goats	75,095	0.048	3604	1081
Donkey, horse, mule, and camel	1370	0.235	322	97
Poultry	311,500	0.003	935	281
Cattle and water buffalo	12,121	0.245	2970	891

2.4 Composition of Lignocellulosic biomass

Lignocellulosic biomass primarily consists of three organic constituents classified as cellulose, hemicellulose, and lignin, which collectively contribute to most of the dry weight of the cell walls of woody and grassy plants (Peterson et al., 2008). These polymers are linked together in a heteromatrix to varied degrees and have different compositions due to the kind of biomass, plant species, and even biomass origin.

In most cases, cellulose fibrils are covered with hemicellulose to create an open network, with lignin eventually filling in the gaps (Lee et al., 2014). Figure 2.4.1 shows the construction of plant cell walls and different bio-compositions.

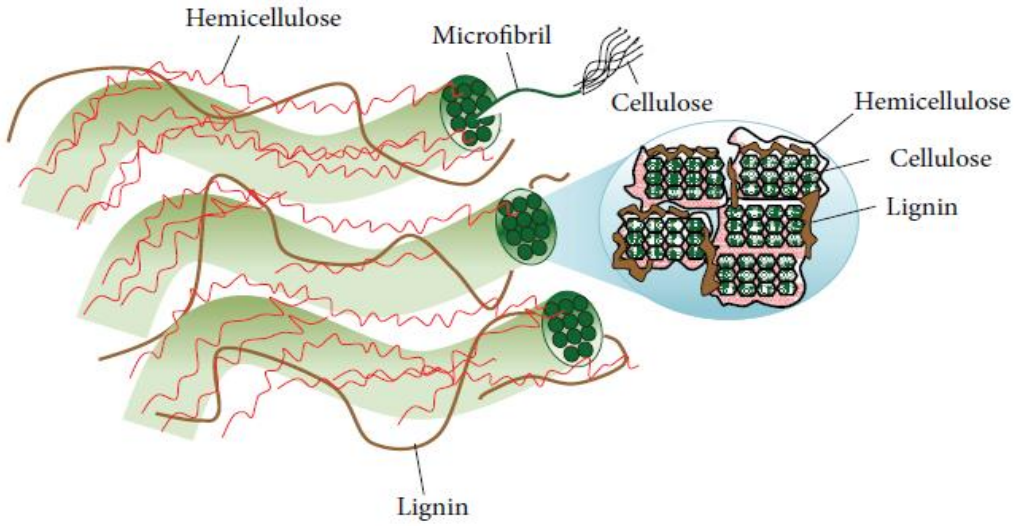

Figure 2.4.1 Structure of plant cell walls and cross-section of microfibrils (Lee et al., 2014).

Commonly, cellulose, hemicellulose, and lignin account for 35–50%, 20–35%, and 10–25%, respectively, of lignocellulosic biomass. Oils, inorganic compounds, proteins, and extractives are also detected in minor quantities in lignocellulosic biomass, albeit none of them plays an important function in the material's structure (Isikgor and Becer, 2015). Table 2.4.1 lists certain lignocellulosic biomass types along with their chemical make-up.

Table 2.4.1 Different lignocellulosic biomass types and their chemical make-up (Isikgor and Becer, 2015).

Lignocellulosic biomass		**Cellulose (%)**	**Hemicellulose (%)**	**Lignin (%)**
Hardwood	Poplar	50.8-53.3	26.2.-28.7	15.5-16.3
	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Softwood				
	Pine	42.0-50.0	24.0-27.0	20.0
	Douglas fir	44.0	11.0	27.0
	Spruce	45.5	22.9	27.9
Agricultural waste	Wheat Straw	35.0-39.0	23.0-30.0	12.0-16.0
	Barley Hull	34.0	36.0	13.8-19.0
	Barley Straw	36.0-43.0	24.0-33.0	6.3-9.8
	Rice Straw	29.2-34.7	23.0-25.9	17.0-19.0
	Oat Straw	28.7-35.6	12.0-29.3	15.4-20.0
	Ray Straw	36.2-47.0	20.0-26.0	10.0-15.0
	Corn Cobs	33.7-41.2	19.0-24.5	9.9-24.0
	Corn Stalks	35.5-39.6	31.9-36.0	6.1-15.9
	Sugarcane Bagasse	25.0-45.0	16.8-35.0	7.0-18.4
	Sorghum Straw	32.0-35.0	28.0-32.0	15.0-25.0
Grasses				
	Grasses	25.0-40.0	25.0-50.0	10.0-30.0
	Switchgrass	35.0-40.0	25.0-50.0	10.0-30.0

✓ Cellulose

Cellulose is a polysaccharide with six carbons (C6) that defines the construction of plant cell walls while also providing mechanical strength and chemical stability. It's a glucose-based unbranched linear polymer that's mostly made up of carbon (44.44 percent), hydrogen (6.17 percent), and oxygen (49.39 percent). Strong intra- and intermolecular hydrogen interactions can ultimately emerge because of the 1,4-glycosidic connections that bind the glucose monomers together. As a result, this main property of cellulose makes it crystalline, resistant to water swelling, and resistant to enzyme assault.

Under normal climatic circumstances (20 °C, 60% relative humidity), cellulose is a relatively hygroscopic substance that absorbs 8-14 percent of the water it comes into contact with. Nonetheless, it is water insoluble and swells when exposed to it. Higher temperatures lead it to become soluble because the

energy discharged is sufficient to rupture the hydrogen bonds holding the molecule's crystalline phase together. Concentrated acids can dissolve cellulose as well, although hydrolysis causes significant destruction of the polymer (Chen, 2014). Figure 2.4.2 shows Chemical structures of cellulose chains

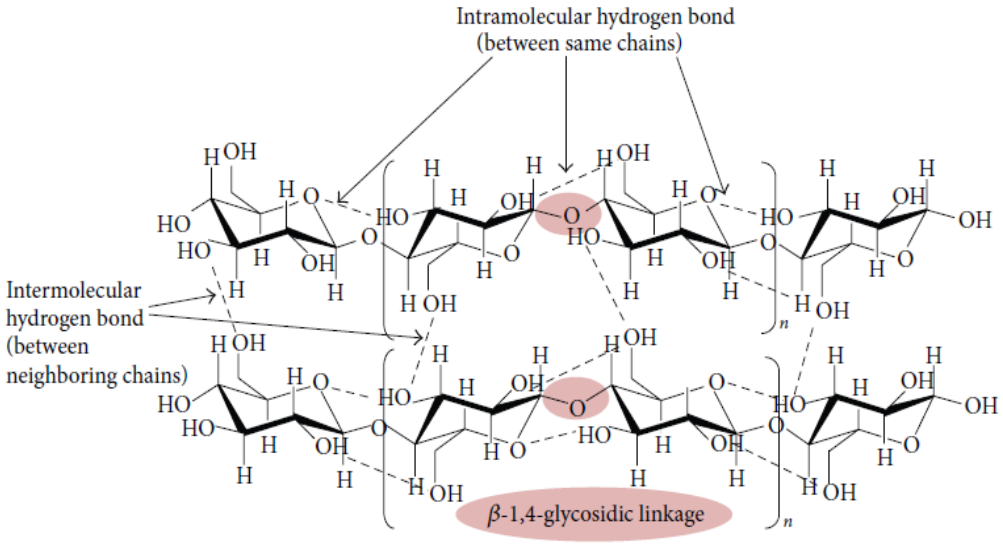

Figure 2.4.2 Chains of cellulose's chemical makeup (Lee et al., 2014).

✓ **Hemicellulose**

Another crucial element of a plant's cell wall is hemicellulose. It is a heteropolymer made up of many different sugar monomers, comprised of mannose, glucose, and xylose. The ratios of these monomers might alter for different feedstock sources and extraction procedures. Xylan, generated from xylose units, is the most prevalent heteropolymer in hardwoods and agricultural plants that contain polysaccharides from the hemicellulose family. Relevant monomers are linked by glycosidic and fructose ether connections to make a branching polymeric structure. This structure of hemicellulose binds lignin and cellulose to form a stiff lignocellulose structure. Hemicellulose lacks recurring b-(1/4)-glycosidic linkage patterns, which is why it does not form a crystalline structure like cellulose does and is thus vulnerable to hydrothermal extraction and hydrolysis.

At low temperatures, hemicellulose is water insoluble. In contrast to cellulose, its hydrolysis begins at a lower temperature, making it soluble at extreme temperatures. The presence of acid greatly enhances hemicellulose solubility in water (Chen, 2014). Figure 2.4.3 shows main components of hemicellulose.

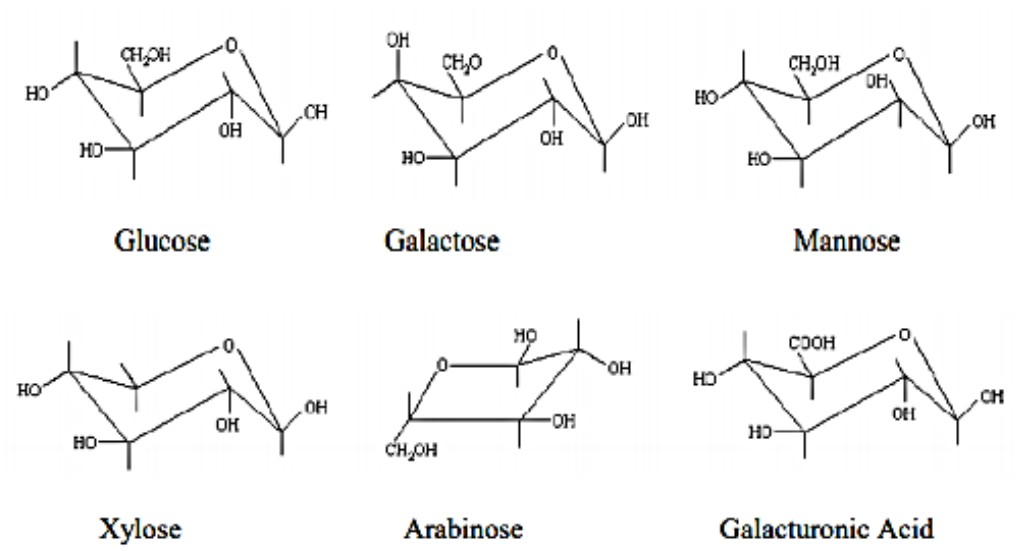

Figure 2.4.3 Principal hemicellulose ingredients (Mohan et al., 2006).

✓ **Lignin**

Lignin is nature's most complicated polymer located in the secondary cellular cell wall, and by simply acting as an adhesive between cells and creating a composite material, it offers exceptionally strong resistance to actual impact, compression, and bending. It is a three-dimensional amorphous polymer made up of several kinds of linkages between phenylpropane molecules. The most frequent motifs include sinapyl alcohol, P-coumaryl alcohol, and coniferyl alcohol.

Seasonal variations, plant age, plant kind, and the extraction and isolation processes all have an impact on the monomer compositions in lignin structures (Roy et al., 2020).

Low molecular alcohols, such as Dimethyl sulfoxide, acetone, pyridine, and dioxane, have been found to dissolve lignin. Thermal softening of lignin

begins at higher temperatures, allowing acidic or alkaline depolymerization processes to proceed more quickly (Harmsen et al., 2010). Figure 2.4.4 shows the chemical structures of lignin.

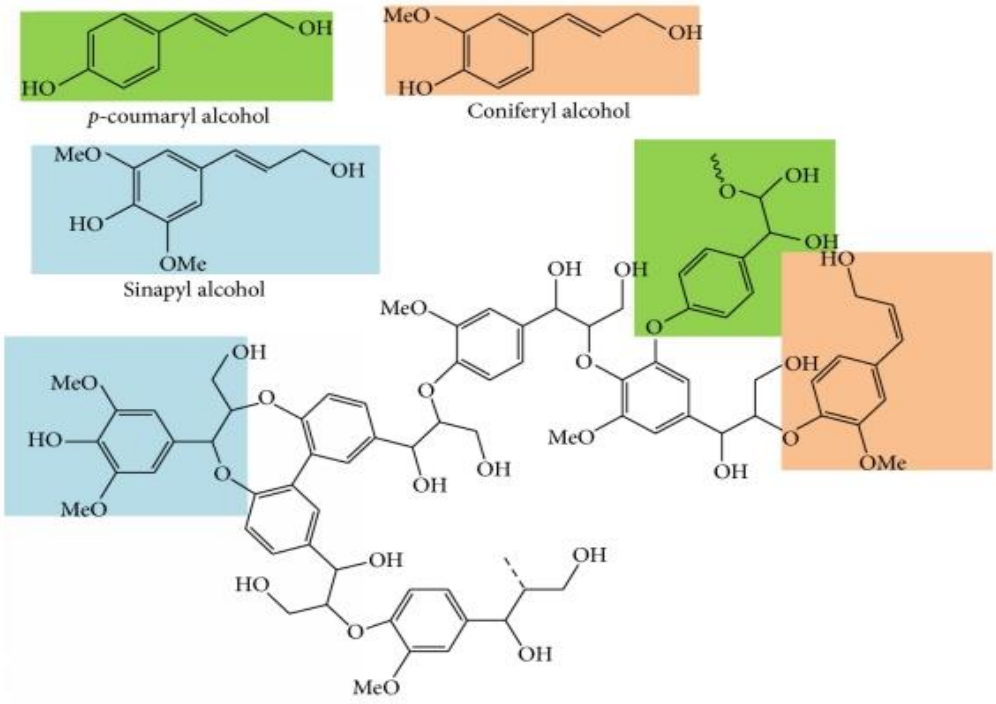

Figure 2.4.4 Lignin's chemical make-up (Lee et al., 2014).

✓ **Inorganic matter**

In general, biomass contains minute quantities of inorganic compounds (ash), the amount of which fluctuates according to the kind of raw material (Alaswada et al., 2015). Metals such as calcium, sodium, potassium, magnesium, phosphorus, silicon, aluminum, and iron are among them. (Werkelin et al., 2005). Water-soluble residues such as chlorides, sulphates, oxalates, nitrates, carbonates, and both organic and inorganic amorphous materials are the most prevalent solid residues found in biomass.

Some pretreatment techniques involve drying biomass at 105 °C before heating it in furnaces to temperatures as high as 750 °C. Under these circumstances, elements like sulfur, nitrogen, oxygen, hydrogen, and carbon evaporate as gaseous molecules due to their chemical properties, while the ash

residue, which comprises mineral elements in their oxide forms, remains (Chen, 2014).

- ✓ **Extractives**

The extractives include waxes, rosin, resin acids, phenols, terpenes, steroids, fatty acids, fatty alcohols, and a variety of other minor organic compounds that are solvent extractable and exist as monomers, dimers, and polymers. Extractive composition varies greatly depending on the species (Rowell et al., 2012).

2.5 Pretreatment Methods of Lignocellulosic Biomass

A critical step in the manufacture of fuels and chemicals is defeating the resistance (Plant cell walls' resilience to tearing) of lignocellulosic biomass. The cellulose's extremely crystalline structure, which is encased in a matrix of polymers made up of lignin and hemicellulose, is what causes the recalcitrance. The primary aims of pretreatment are to get rid of this resistance, to disentangle cellulose from the matrix polymers, and to increase its accessibility for hydrolysis.

Pretreatment methods are often divided into four distinct groups: biological, chemical, physical, and physicochemical. Pre-treatment results vary depending on the technique, biomass, and process parameters used. All pre-treatment techniques enhance the amount of surface that is accessible, but only a few can depolymerize lignocellulosic polymers and are efficient for hemicellulose separation, lignin removal, and lignin structure modification.

Table 2.5.1 lists the benefits and drawbacks of several lignocellulosic biomass pre-treatment techniques. Table 2.5.2 shows how various approaches affect the chemical composition and structural changes in biomass.
The following are examples of chemical pretreatments:

2.5.1 Alkaline.

Utilizing bases like Ammonium hydroxide, potassium, calcium, and sodium for the preparation of lignocellulosic biomass is known as an alkaline pretreatment. The application of an alkali results in the degradation of ester and glycosidic side chains, shifting the lignin's structure, causing cellulose to swell, partially decrystallizing cellulose, and partially solvating hemicellulose. Alkaline pretreatment often involves fewer extreme conditions than other pretreatments. Although it may be done at ambient temperatures, pretreatment times must be greater than they are at higher temperatures The biomass is submerged in alkaline solutions during the alkaline process and followed by mixing at a specified temperature for a particular amount of time.

2.5.2 Wet Oxidation.

In wet oxidation, oxygen is used to oxidize substances that are dissolved in water. Two responses happen throughout this operation. The first is a high-temperature oxidation process, while the second is a hydrolysis reaction at low temperatures. After the material has dried and been ground into 2 mm-sized particles, wet oxidation normally entails adding water. To reduce the development of byproducts, a chemical, often Na_2CO_3, is added to the mixture and Up until a pressure of 12 bar is attained, air is injected into the vessel. This pretreatment technique is carried out at 195°C for ten to twenty minutes. By eliminating lignin and solubilizing hemicellulose, wet oxidation can be utilized to fractionate lignocellulosic material. Lignin breaks down into water, carboxylic acids, and carbon dioxide during wet oxidation. Depending on the kind of biomass processed and the circumstances utilized, the quantity of lignin eliminated following pretreatment varies from 50% to 70%.

2.5.3 Acid.

During the acid pretreatment process, the lignocellulosic material's rigid building is taken apart by the application of concentrated and diluted acids. Switchgrass, maize stover, spruce (softwood), and poplar have all been

commercially pretreated with diluted sulfuric acid (H_2SO_4), the most commonly used acid. Diluted sulfuric acid has traditionally been used to make furfural. Hemicellulose is hydrolyzed to simple sugars like xylose, which then proceeds to transform into furfural. Numerous other acids, including hydrochloric acid, phosphoric acid, and nitric acid have also been researched (HNO_3). Acid pretreatments have been put to use as a part of overall procedures in separating the lignocellulosic biomass's constituent parts because of their capacity to remove hemicellulose. A reasonably pure form of cellulose is produced by first pretreating with an acid to remove the hemicellulose and then pretreating with an alkali to remove the lignin. This chemical pretreatment typically involves mixing the biomass continuously at temperatures ranging from 130 °C to 210 °C while adding concentrated or dilute acids (often between 0.2 percent and 2.5 percent w/w) to the biomass. The time it takes to hydrolyze the sugars may take a short while to many hours, based on the conditions around the pretreatment.

2.5.4 Green Solvents.

Salts known as ionic liquids frequently include a tiny anion and a big organic cation and have an extremely low vapor pressure. Corn stover, cotton, bagasse, switchgrass, wheat straw, and woods of various hardness can all be dissolved by adjusting the anion and cation's chemistry to produce a broad range of liquids (pine, poplar, eucalyptus, and oak). They are said to be "green solvents" because no hazardous byproducts are produced during the pretreatment process, and because ionic liquids (IL) can be recovered. In addition to having a high dissolving capacity, an IL should also have a low melting point, low viscosity, minimum or no toxicity, and excellent stability in order to be utilized in biomass pretreatment. As part of the IL pretreatment process, at moderate pressures and temperatures of 90–130 °C, biomass is dissolved in the solvent for periods of up to 24 hours. Prior to enzymatic hydrolysis, the biomass is first reprecipitated by adding water and repeated washings. An anion of the IL forms 1:1 hydrogen links with cellulose (sugar hydroxyl protons), disintegrating cellulose's crystalline hydrogen-bonded structure and further amorphizing it, making it vulnerable to enzymatic hydrolysis. Additionally, the chemistry of the IL may be adjusted to

cause the lignin and hemicellulose to breakdown, making it appropriate to dissolve the various components (Brodeur et al., 2021).

Table 2.5.1 Advantages and drawbacks of various lignocellulosic biomass pretreatment techniques (Brodeur et al., 2021).

Pretreatment methods	Advantages	Disadvantages
Alkali	(i) Efficient removal of lignin (ii) Low inhibitor formation	(i) High cost of alkaline catalyst (ii) Alteration of lignin structure
Acid	(i) High glucose yield (ii) Solubilizes hemicellulose	(i) High costs of acids and need for recovery (ii) High costs of corrosive resistant equipment (iii) Formation of inhibitors
Green solvents	(i) Lignin and hemicellulose hydrolysis (ii) Ability to dissolve high loadings of different biomass types (iii) Mild processing conditions (low temperatures)	(i) High solvent costs (ii) Need for solvent recovery and recycle
Steam	(i) Cost effective (ii) Lignin transformation and hemicellulose solubilization (iii) High yield of glucose and hemicellulose in two-step process	(i) Partial hemicellulose degradation (ii) Acid catalyst needed to make process efficient with high lignin content material (iii) Toxic compound generation
LHW	(i) Separation of nearly pure hemicellulose from rest of feedstock (ii) No need for catalyst (iii) Hydrolysis of hemicellulose	(i) High energy /water input (ii) Solid mass left over will need to be dealt with (cellulose/lignin)
AFEX	(i) High effectiveness for herbaceous material and low lignin content biomass (ii) Cellulose becomes more accessible (iii) Causes inactivity between lignin and enzymes (iv) Low formation of inhibitors	(i) Recycling of ammonia is needed (ii) Less effective process with increasing lignin content (iii) Alters lignin structure (iv) High cost of ammonia
ARP	(i) Removes majority of lignin (ii) High cellulose content after pretreatment (iii) Herbaceous materials are most affected	(i) High energy costs and liquid loading
Supercritical fluid	(i) Low degradation of sugars (i) Cost effective (iii) Increases cellulose accessible area	(i) High pressure requirements (ii) Lignin and hemicellulose unaffected

Table 2.5.2 Effect of different pretreatment techniques on lignocellulosic biomass's chemical composition and chemical/physical structure.
H: high effect, L: low effect, ND: not determined (Brodeur et al., 2021).

Pretreatment	Increase accessible surface area	Decrystallizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Steam explosion	H		H		L
Liquid hot water	H	ND	H		L
dilute acid	H		H		H
AFEX	H	H	L	H	H
ARP	H	H	L	H	H
Lime	H	ND	L	H	H
Green solvents (NMMO and ionic liquids)	H	H	L	H or L	L
Supercritical fluid	H	H	H		L

2.6 Thermochemical Conversion Technologies

Thermochemical conversion is among the most essential processes in converting biomass into useful chemicals or biofuels. This kind of method uses the application of heat and chemical reactions to produce energy. Pyrolysis, gasification, liquefaction, and combustion are the four thermochemical conversion processes.

✓ Combustion

The combustion processes provide roughly 90% of all renewable energy derived from biomass. Wood, dry leaves, hard vegetable shells, rice husks, dried animal excrement, and other biomass can be burned in combustion plants (Lebaka, 2013). In the combustion process, oxygen and biomass are mixed in a hot atmosphere to generate CO2, water vapor, and heat (**Eqs. 1** and **2**).

Biomass + Oxygen → Carbon Dioxide + Water + Heat Eq. 1

The approximate chemical equation for biomass combustion is:

$$CH_{1.44}O_{0.66} + 1.03\ O_2 \rightarrow CO_2 + 0.72\ H_2O + \text{Heat} \qquad \text{Eq. 2}$$

The kind of biomass utilized in the process, which is one of several factors that affect how much heat is generated, is crucial, however the average thermal energy produced is 20 MJ/kg of biomass (Nussbaumer, 2003). Equations 1 and 2 demonstrate that combustion is an exothermic chemical reaction, in which the biomass is burned while exposed to air, releasing chemical energy that may then be transformed into mechanical and electrical energy (Lebaka, 2013; Kaushika et al., 2016). The combustion process occurs inside combustion chambers within the temperature range of 800-1000 °C. Moisture percentage, which ought to be lower than 50%, is a crucial condition for the dry biomass utilized. With associated electrical efficiency of 25–30%, biomass combustion plants—which use wood and forest leftovers as fuel—typically produce between 20 and 50 Mwe (McKendry, 2002).

- ✓ **Pyrolysis**

The technology of partially combusting a certain type of biomass at roughly 500 °C without oxygen to produce liquid (bio-oil), solid (charcoal), and gaseous (combustible gas) products is called pyrolysis. The volatile parts of the gases that produce biomass may be vaporized at high temperatures, and their vapors can then be liquefied to form liquids. The liquid fuel that is produced by this procedure can be kept and utilized for a variety of heating and electricity-producing purposes. In addition to producing liquid fuel, the pyrolysis process also creates other combustible products, including charcoal, gas, and several other high-value compounds. Figure 2.6.1 depicts the usual layout of the biomass pyrolysis procedure for energy (Lebaka, 2013; Kaushika et al., 2016).

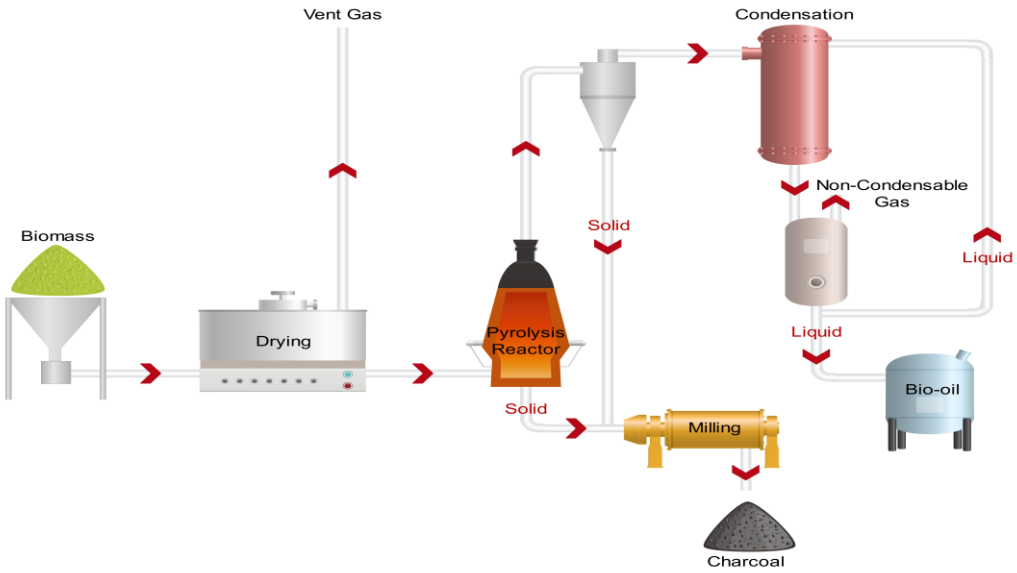

Figure 2.6.1 Biomass pyrolysis scheme (Tursi, 2019).

In contrast to basic pyrolysis systems, which function at temperatures lower than 600 °C, industrial facilities operate between 600 and 1000 °C, producing gas with a greater hydrogen content. Of course, these procedures also call for more advanced management and systems (Di Blasi, 2008).

The pyrolysis procedure involves four key phases, and they happen in the sequence listed below at various temperatures (Portha et al., 2017)

a. The first step is to dry the incoming biomass between 100 and 120 °C.

b. Distilling acetic acid, methanol, and the output gases (mostly N_2, CO, and CO_2) at 275 °C.

c. Exothermic reactions occur between 280 and 350 degrees Celsius., shattering the weakest chemical bonds to release CO_2, (CO), (CH_4), C_2H_6, and H_2 from complicated combinations of chemicals.

d. Evaporation at 350 °C to remove all volatile chemicals; larger amounts of H2, CO, and carbon are formed; the final one is left behind as leftovers in the form of charcoal.

Various techniques are available to use the pyrolytic process that effects the creation of bio-oil, syngas, and carbonaceous residues.

I. Carbonization is the most ancient and well-known pyrolysis process, occurring in the 300-500 °C temperature range. Only a solid portion (vegetable coal) is obtained from this method.

II. Approximately three fractions are produced in equal amounts by slow or conventional pyrolysis, which takes happening at 500 °C temperatures. Since slow pyrolysis occurs at low temperatures and heating values, it necessitates longer reaction and transformation durations than fast pyrolysis.

III. Fast pyrolysis occurs at medium-low temperatures (500 to 650 °C), where the gasification processes occur fast and with short contact durations, reforming the intermediate compounds and increasing the liquid fraction output to 70–80 wt.% of the incoming biomass. The final products of this particular pyrolysis are typically 60 percent of the bio-oil, 20 percent of the bio-coal, and 20 percent of the gas.

IV. Flash pyrolysis is accomplished at temperatures above 650 °C with less-than-second contact times and favors the generation of the gaseous fraction (up to 80% efficiency) (Kaltschmitt, 2019).

- ✓ **Gasification**

The gasification process turns solid carbon sources (solid biomass) into synthesis gas, often known as syngas, that is mostly comprised of CO, hydrogen (H2), and nitrogen (N_2) (Rahimpour et al., 2012). Procedure is the partial oxidation of the solid matrix at high temperatures (Molino et al., 2016). Following gasification, the gas is "cleaned" to simultaneously recover trace elements and eliminate contaminants. Due to its capacity to completely purge the syngas of all contaminants, gasification is a particularly intriguing technique, especially when it comes to materials containing a lot of heteroatoms or other impurities that can't be handled using conventional methods. According to the biomass kind and the process' operating circumstances, the generated gas is divided into a number of combustible and non-combustible fractions. The generated gas typically has a calorific value of 4.5 to 6 MJ/m^3, which is equal to 10 to 50% of natural gas's calorific content (Akia et al., 2014).

- ✓ **Liquefaction**

At high pressures and moderate temperatures (between 280 and 370 °C), liquefaction is a method utilized to convert biomass (10–25 MPa). As well as numerous gaseous, aqueous, and solid by-products, a liquid biogranulate that resembles crude oil is also produced (López Barreiro et al., 2013). The ultimate outcome is a fuel that is chemically stable since it has a high heating capacity and less oxygen. Liquefaction's principal purpose is to produce oil with a high H/C ratio. Based on the raw materials employed, two procedures are recognized for this sort of conversion: algal biomass (wet raw material) and lignocellulosic biomass (dry raw material) liquefaction. In both situations, the raw material needs to undergo a preparatory treatment that entails the elimination of woody biomass impurities and the creation of a stable suspension, leading in a decrease in particle size (via alkaline treatments), enabling straightforward pumping into reactors (Gollakota et al., 2018). The most common strategy is to use lignocellulosic biomass that has been treated at 350 °C and 150 bar pressure for around 15 minutes. Under these processing circumstances, a spontaneous phase separation occurs, resulting in a CO2 gaseous phase, solid waste, bio-crude, and a little aqueous phase (Rowbotham et al., 2012). The material that was recovered in the solid phase might be used right away as fertilizer or biofuel. Inside the plant, the aqueous phase could be utilized for water-dependent activities or anaerobic digestion. To be used economically, the resulting bio-crude, which has a low oxygen concentration, needs to be refined further (Yu et al., 2011).

2.7 Subcritical Water

In hydrothermal liquefaction, water not only reacts but also functions as a catalyst. In general, subcritical water is regarded as a solvent for converting biomass as it enables (Möller, 2011).

When water approaches the critical point, it takes on a variety of intriguing characteristics. a high level of organic solubility and low viscosity are two of them, making subcritical water a great medium for rapid, homogeneous, and effective procedures (Toor et al., 2011).

Subcritical water, also referred to as superheated water or pressured hot water, is defined as water varying from 100 °C to 374 °C in temperature (critical temperature) and a pressure higher than its vapor saturation, up to 22.1 MPa, to maintain the water's state of liquidness. Supercritical water is a fluid having a greater temperature and pressure than its critical point (374 °C, 22.1 MPa) (Gbashi et al., 2017).

Figure 2.7.1 depicts the water's subcritical and supercritical zones (Cardenas-Toro et al., 2014).

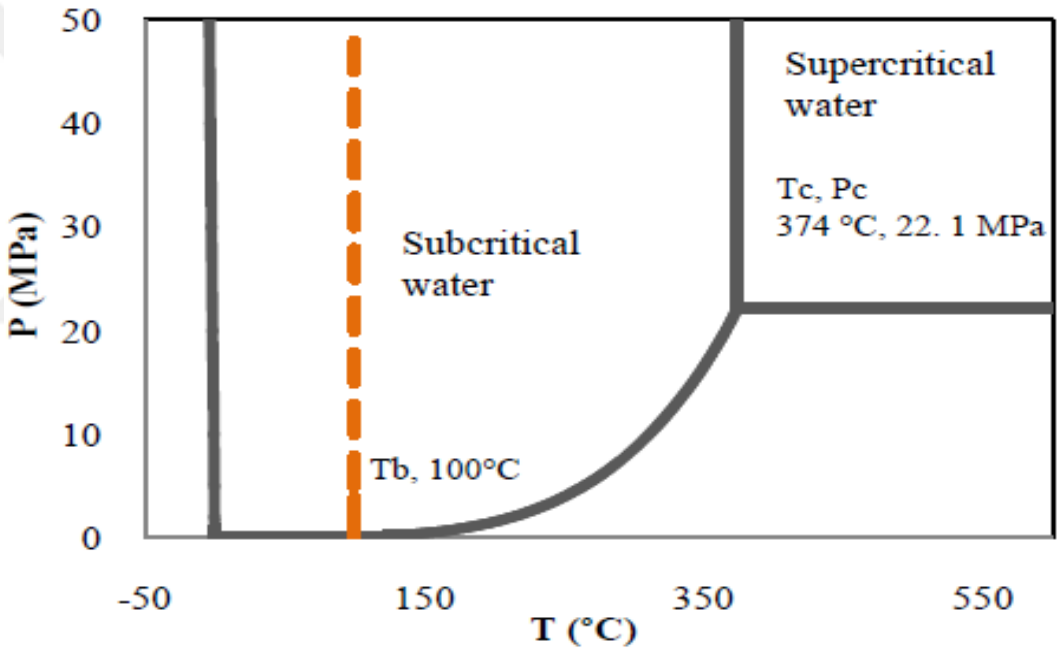

Figure 2.7.1 Temperature and pressure-dependent water phase diagram (Cardenas-Toro et al., 2014).

in comparison to typical circumstances, the physicochemical parameters of subcritical and supercritical water, like ionic products, dielectric constant, density, and viscosity, all vary drastically when both pressure and temperature rise.

The physicochemical characteristics of water at subcritical and supercritical situations are shown in Figure 2.7.2. (Cardenas-Toro et al., 2014).

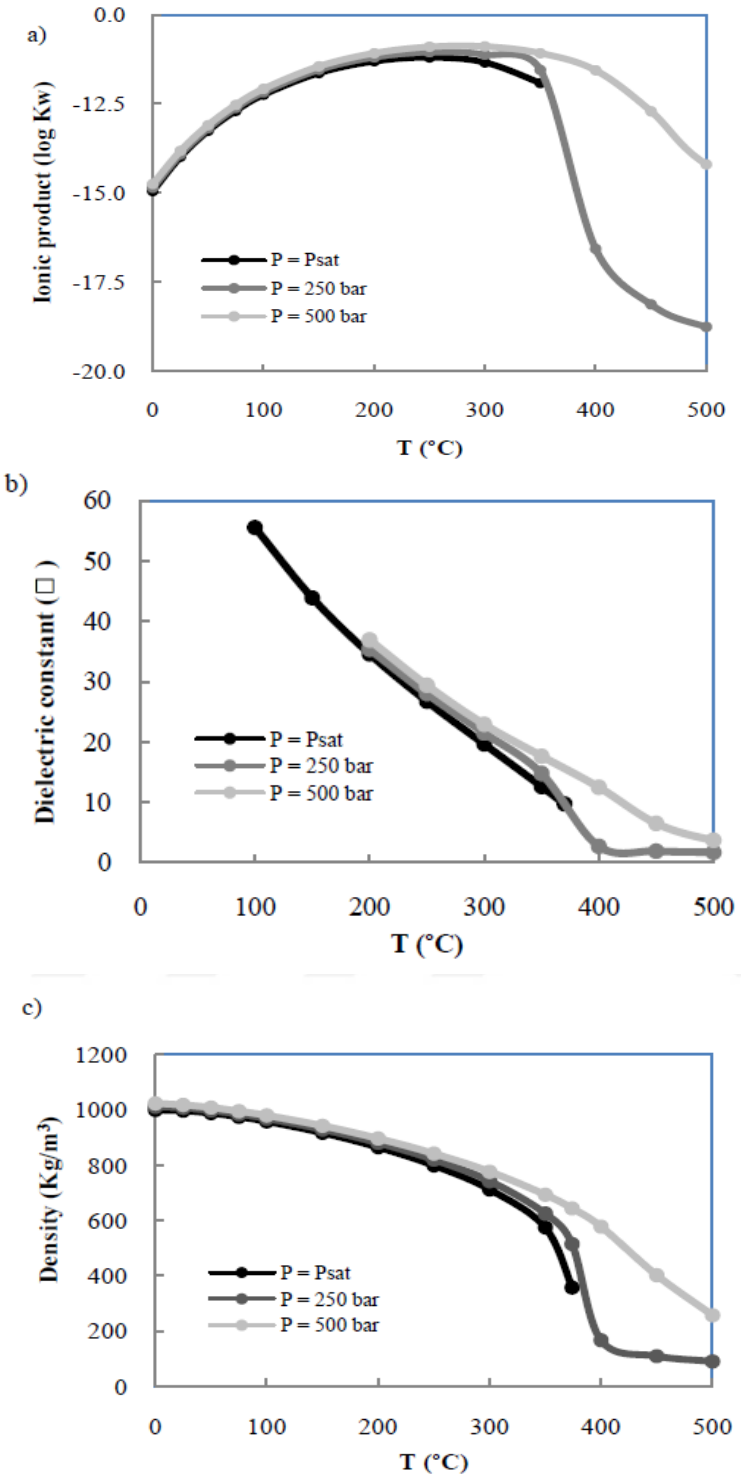

Figure 2.7.2 Water's physicochemical characteristics in subcritical and supercritical circumstances: (a) Ionic product, (b) Dielectric constant, (c) Density (Cardenas-Toro et al., 2014).

The physicochemical qualities of water are greatly impacted by temperature; for instance, water's dielectric constant decreases from 35 at 200 °C

to 10 at 374 °C when hydrogen bonds are ionized at extreme temps. This attribute of water allows it to be particularly suitable for organic reactions in subcritical and supercritical states, and the miscibility of organic molecules improves with temperature.

Furthermore, the concentration of water's ionic product (Kw = [H+][OH-]) is three times larger under these parameters than under normal circumstances, revealing that it behaves as an acid-base catalyst.

Additionally, the density of water drops as the temperature rises, from 1000 kg/m^3 at 25°C to 820 kg/m^3 at 250°C and 25 MPa.

Because of the interplay of these factors, solvation power is temperature dependent, with high temperatures near the supercritical point resulting in a high amount of water dissociation and decreased density.

These variables affect chemical processes' selectivity as well as their kinetics within a network of reactions and are mostly considered catalytic in nature (Cardenas-Toro et al., 2014).

2.8 Functional groups of lignocellulose components and its conversion to the chemicals

In terms of production of sugar monomers from lignocellulose and other worthy chemicals, the relevant functional groups are:

1.Functional groups implicated in the hydrolysis of polysaccharides to monomers and potential degradation processes of these corresponding monomers (e.g. to furfural).
2. Functional groups that break down lignin (partially) into fragments or phenolic substances so that enzymes can reach the cellulose portion. Table 2.8.1 lists the functional groupings of all three components.

Table 2.8.1 Functional groups in lignocellulose components (Harmsen et al., 2010)

Functional Group	**Lignin**	**Cellulose**	**Hemicellulose**
Aromatic ring	X		
Hydroxyl group	X		
Carbon to carbon linkage	X		
Ether (glucosidic) Linkage	X	X	X
Ester bond			X
Hydrogen bond*		X	X

Various functional groups in the lignin polymer contribute to depolymerization and degradation, ultimately leading to water-soluble derivatives. When it comes to cellulose, the notable focus is on glucosidic (ether) bond rupture, leading to the formation of sugar monomers (Harmsen et al., 2010).

The usual pathways for lignocellulosic biomass transformation include the following procedures:

(1) Lignocellulosic biomass disintegration,
(2) cellulose/hemicellulose hydrolysis into C5 (mostly xylose)/C6 sugars (glucose),
(3) glucose to fructose isomerism,
(4) xylose's dehydration into FF,
(5) Fructose dehydration to 5-HMF,
(6) converting FF to furfuryl alcohol by hydrogenation, and
(7) Hydration of 5-HMF, hydrolysis, and rearrangement of furfuryl alcohol to produce LA (Lin et al., 2022).

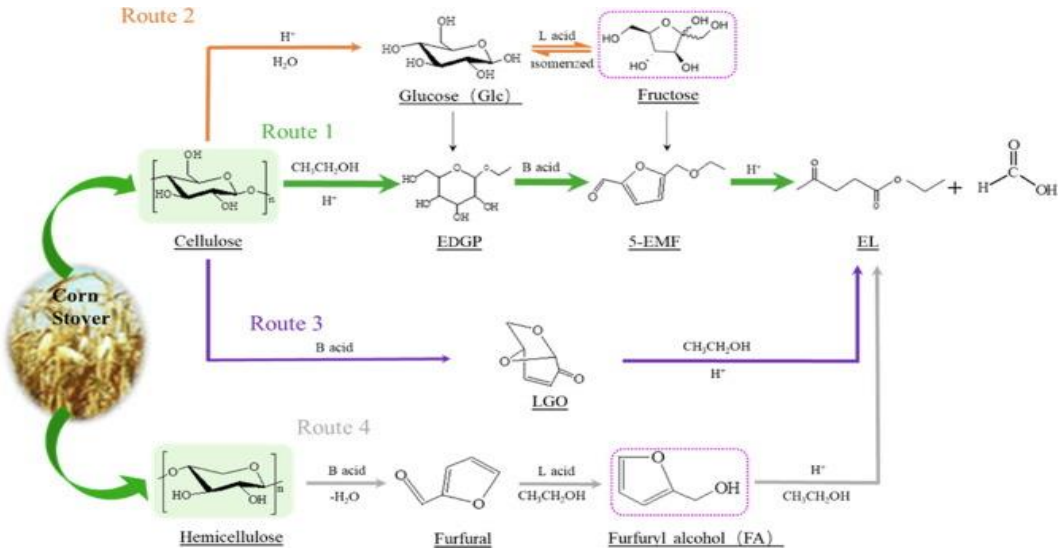

Figure 2.8.1 Mechanism of biomass conversion to various platform chemicals (Lin et al., 2022).

3. LITERATURE REVIEW

Lignocellulosic biomass has generated interest since it is renewable, and because there are fewer stocks of crude oil, there is a renewed emphasis on biomass as a substitute energy supply. The recovery of platform chemicals and the possibility for bio-oil from biomass material is heavily reliant on the conversion of cellulose, which is crucial feature of biomass.

Cellulose is a glucose polymer with a very high polymerization, consisting of 10,000 glucose reparative units linked to one another by 1,4 glycosidic units. Biomass depolymerization is a mass- and heat-transfer process because of the robust inter- and intramolecular hydrogen interactions in the lignocellulosic structure and the pretreatment of lignocellulosic biomass is recognized as one of the probable strategies for cellulose depolymerization. (Malaspina and Faraudo, 2019).

It is necessary to pretreat lignocellulosic biomass to improve the solid structure's surface area and achieve cellulose decrystallization, resulting in the elimination of hemicellulose and lignin portion. Numerous methods for pre-treating lignocellulosic biomass, including steam explosion, hot water application, diluted acid, lime, ionic liquids, and co-solvent application, have been recorded in scholarly works, and pretreatment effects differ depending on the approach utilized, the process variables used, and the kind of biomass employed. Although all pre-treatment treatments increase accessible surface area, only a few approaches may depolymerise lignocellulosic polymers and be useful for hemicellulose separation, lignin removal, and lignin structure modification. Ionic liquids as green solvents have the tendency to reduce crystalline structure, but they are ineffective for separating hemicellulose. On the other hand, whereas supercritical liquid application is highly successful for decrystallization and hemicellulose separation, it has a limited impact on lignin structure. In order to produce bioethanol and extract platform chemicals, lignocellulosic biomass must first undergo pre-treatment operations (Brodeur et al., 2021).

Solvent handling makes it feasible to depolymerize cellulose. The polarity, dielectric constant, and solubility characteristics of the solvent all affect its efficiency. Unquestionably, one of the most important aspects for high polymer solubility is the solubility parameter. To attain high dissolution performance, the cellulose polymer's and the characteristics of the solvent's solubility should be as close as feasible.

The process of saccharifying raw biomass is crucial yet difficult due to cellulose's insoluble nature in the majority of solvents. Utilizing a co-solvent can accelerate the dissolution and depolymerization of cellulose, and the operating temperature affects the molecular weight of fragmented oligomers.

Zhicheng Jiang and coworkers examined the impact of sodium chloride on cellulose solubilization and depolymerization in various raw biomass materials in water. According to the findings, a green NaCl-H_2O system considerably improved the solubility and depolymerization of cellulose from unprocessed biomass. In the absence of NaCl, at 220 °C, most of the cellulose was still present in the reaction residue. With the addition of 20 wt percent NaCl the conversion of cellulose in four different types of raw material greatly enhanced. At various temperatures, the impact of NaCl on cellulose conversion was examined. Higher reaction temperatures led to a greater amount of cellulose conversion being seen. As a consequence, at 220 °C, adding 20 wt % NaCl significantly boosted the conversion of cellulose in pubescen from 58.1 to 99.0 percent, as opposed to increasing from 21.6 to just 27.5 percent at 180 °C. Additionally, the impact of NaCl concentration on cellulose conversion was assessed. As stated in the article, by only incorporating a modest amount of NaCl, the cellulose conversion in each of the four categories of basic materials rose dramatically. The cellulose in pubescen, maize stover, and corncob residue was almost entirely converted when the NaCl content was raised to 10 weight percent, while the cellulose in mulberry wood was converted to up to 76 percent. The amount of cellulose conversion did not rise further even after adding more NaCl (20 wt percent). This work used ESI-MS and gel permeation chromatography to specify the molecular weight of liquid items following treatment in the NaCl-H2O system. The results showed that for diverse raw materials, NaCl significantly enhanced the depolymerization of

cellulose into oligomers in biomass, with molecular weights of 200-400 Da, as well as its solubilization and improved the breakdown of hydroxymethylfurfural to give levulinic and formic acids. FTIR spectroscopy was a different analysis that this study looked at. It served to characterize the solid residues and the raw materials. In light of this, the results demonstrated that $C\bar{I}$ severely damaged the intermolecular hydrogen bond, which had an FTIR band at about $\tilde{\nu}=3200cm^{-1}$. As $C\bar{I}$ could interact significantly on a 1:1 basis with the end-OH group of the glucose unit, intermolecular and intramolecular hydrogen bonding could disintegrate more rapidly (Jiang et al., 2015).

Jie Cai and Lina Zhang examined the breakdown of cellulose in water-based solutions of LiOH and urea as well as NaOH and urea. They employed four different types of cotton linter pulp as cellulose samples. To examine the dissolving capability of solvents, aqueous solutions of 4.2% LiOH/1.12% urea, 7% NaOH/1.12% urea, and 9.8% KOH/1.12% urea, that is, 0.175 mol alkali hydroxide/0.2 mol urea, were used in this research. Throughout the experimental phase, cellulose was dissolved in a 10 °C pre-cooled solvent. while being stirred during the time period specified. To be able to extract recovered cellulose, the mixed solution was then promptly precipitated from the aqueous solution into diluted acetic acid. Through the use of 13CNMR, optical microscopy, wide-angle X-ray diffraction (WAXD), FT-IR spectroscopy, DSC, and viscometry, the dissolving behavior and solubility of cellulose were assessed. LiOH/urea, followed by NaOH/urea, and then KOH/urea aqueous solution, had the highest dissolving power. According to the findings of DSC and 13C NMR, the non-derivatizing solvents LiOH/urea and NaOH/urea disrupted the intra- and intermolecular hydrogen bonds of cellulose and prevented the cellulose molecules from approaching one another, resulting in a good dispersion of cellulose to create a real solution. (Cai and Zhang, 2005)

The processing of lignocellulosic biomass with acetone has been studied in several literature sources. With a solubility parameter (δ value) of 9.9 $cal^{1/2}\ cm^{-3/2}$, which is analogous to that of acetic acid, it is the most preferred ketone.

For the purpose of efficiently using each component in the thermo-chemical conversion of biomass, Isao Hasegawa and colleagues have researched pretreatment techniques for separating hemicellulose, cellulose, and lignin from biomass. As a lignocellulosic feedstock and solvent, respectively, they employed oil palm shell wastes and water/acetone. They used two distinct strategies., the first of which was a two-step procedure and the second of which just required one. Hemicellulose, lignin, and cellulose portions of biomass were easily separated after being treated with hot water at 180 °C. followed by extraction with a stream of water/acetone under 10 MPa at 230 °C. With the assist of the hot water treatment, hemicellulose found in biomass was effectively retrieved as saccharides, perhaps leaving lignin and cellulose in their solid state. Lignin was depolymerized into compounds soluble in water/acetone employing a water/acetone solvent combination, and remaining cellulose was partially dehydrated. The other approach was a one-step procedure in which a batch reactor directly extracted biomass at 200 °C using a 50/50 solution of water and acetone, leaving just pure cellulose as a residue (Hasegawa et al., 2004).

Researchers Edgardo Araque and colleagues investigated the organosolv pretreatment for generating ethanol from Pinus radiata D. Don. In a reactor filled with wood chips (basis on dry weight) and a 50:50 (v/v) acetone: water combination with sulfuric acid as catalyst (0.9 percent w/w dry wood pH 2), organosolv pretreatment was conducted. Within the reactor, the solvent: wood ratio was 7:1 (w/w). To evaluate the experimental parameters in this investigation, a factorial analysis was undertaken, and the values were then optimized for the highest possible yield via enzymatic hydrolysis. Temperature (183-197 °C) and time (4-46 min) were assessed for their impact. At the various tested temperatures, the attained pressures varied from 2.00 to 2.34 MP. The greatest yield for bioethanol synthesis was over 99.5% (36 g/L) from an organosolv pretreated material generated at 195 °C, 5 minutes, and pH 2.0 (Araque et al., 2008).

A unique approach for fractionating lignocellulosic biomass was investigated by Yi-Heng Percival Zhang and colleagues based on the varied solubility and volatility of cellulose, hemicellulose, and lignin with various solvents. As lignocellulosic biomass feedstock, they employed hybrid poplar,

switchgrass, and corn stover. To dissolve cellulose, hemicellulose, and lignin, the procedure successively employed acetone as a very volatile organic solvent, water, and a concentrated phosphoric acid as nonvolatile cellulose solvent under mild response circumstances (50°C and atmospheric pressure). As a result, although cellulose was soluble in concentrated phosphoric acid, it was insoluble in water. due to its high solubility in an acetone/water solution, hemicellulose was separated from cellulose. Because lignin was soluble in organic solvents but insoluble in aqueous solutions, it could be isolated from other lignocellulose ingredients. The greatest enzymatic cellulose digestibility (97%) occurred during the hydrolysis stage at enzyme loadings of 15 cellulase filter paper units and 60 IU of beta-glucosidase per gram of glucan, which were attributed to the minimal sugar degradation during fractionation and the best enzymatic cellulose digestibility (97%) during the hydrolysis stage. (Zhang et al., 2007).

Junnienkul and colleagues looked at the saccharification of rice straw. Based on Response Surface Methodology (RSM), various different treatment circumstances were gainfully employed to two distinct types of ionic liquids, 1-Ethyl-3-methyl imidazolium chloride and 1-Butyl-3-methyl imidazolium chloride (BMIM-Cl) (EMIM-Cl), and their pretreatment efficiencies were compared. Temperature of 139 °C, reaction time of 88 minutes, and solid loading of 5.2 percent were discovered to be the ideal conditions for [BMIM]Cl treatment. The ideal conditions for [EMIM]Cl treatment were discovered to be temperature 140 °C, reaction duration 72 min, and solid loading 5 percent (Junnienkul et al., 2018).

4. MATERIAL AND METHOD

4.1 Material

In this research, almond shells, which are extensively produced in our nation and have the fifth-highest global output rate, were picked as a genuine biomass feedstock. After supplying almond shells, the dried biomass samples were ground with an MFIKA brand rotary miller to a particle size of 0.5 mm after being air dried.

A Leco CHNS-932, MI, USA elemental analyzer was used to analyze almond shells' constituent elements. the findings are shown in table 4.1.1.

Table 4.1.1 Elemental analysis results of almond shells

Elements (% wt)	**Almond shells**
C	48.83
H	6.91
N	0.01
S	0.02
O	43.46
Moisture	7.70
Ash	0.92

Besides elemental analysis of almond shells, the Van Soest methodology was also applied to identify the structural constituents of biomass, which included cellulose, lignin, and hemicelluloses. Table 4.1.2 provides an illustration of the outcomes. It consists of three operational stages:

NDF: Neutral Detergent Fiber: Total amount of cellulose, hemicellulose and lignin

ADF: Acid Detergent Fiber: Total amount of cellulose and lignin

ADL: Acid Detergent Lignin: Total amount of lignin

Table 4.1.2 The composition of almond shells

Components (daf, wt%)	Almond shells
Total Extractives	4.37
Cellulose	43.06
Hemicellulose	23.32
Lignin	28.80

Experiments were conducted in water and water-ethyl acetate, water-acetonitrile, and water-acetone combination as a solvent.

4.2 Method

This section addresses the experimental systems, experimental procedures, as well as product analysis methodologies.

4.2.1 Experimental System

Experiments about the saccharification of almond shells by chemical pre-treatment were performed in a multiple autoclave reactor system with a 50 mL capacity, which has pressure, temperature, control parts, and sampling connections.

The following are the device's additional specifications:

- There are three 50 mL-capacity vessels in the reactor.
- Reactor chambers can sustain pressures of up to 150 bar.
- 316 stainless steel is utilized to construct reactor chambers.
- There is a Teflon sample chamber to be replaced in the stainless-steel reactor.
- A temperature sensor is installed in each reactor.
- A mechanism for controlling the reactor's temperature is installed.
- Liquid samples can be gathered from the reaction media using a dip tube.
- Reaction systems have a tolerance for temperatures up to 250 °C.
- A magnetic bar is utilized for mixing the reactor.

- Reactor mixing rates are programmable.
- The internal pressures of the reactor are shown via the manometer.
- Reactors have gas discharge valves.
- Reactors are heated by heating jacks.

Figure 4.2.1.1 Reactor system

4.2.2 Experimental Procedure

This study looked at how solvents influenced alterations in the rigid makeup of biomass and also the conversion to sugar by processing of the selected biomass sample in the presence of selected solvents.

Hydrothermal conversion of almond shells was carried out in a number of batch reactors. The biomass sample and solvent (water, ethyl acetate, acetone, and acetonitrile in water in the proportion of 1:1) were put inside the autoclave reactors with a water (solvent)/solid ratio of 2 g solid/18 mL solvent. The system was subsequently closed, and the air within the reactor was flushed out with an inert gas stream (N2) and the valves were closed, consequently inert gas was trapped in the reactor. The reactors were then quickly heated to operating temperature (180 ° C) and studies were conducted at this temperature for 20-40 and 60 minutes. Samples were obtained from a dip pipe near the top of the reactors at the times mentioned when the reactors' temperature reached the specified point. At the conclusion of procedure, the reactors were cooled down rapidly to an ambient temperature. Next, the glass main chamber was pulled

within the open platform, thus inhibiting the development of both the main and secondary responses.

In our multi-reaction system, the reaction was halted by pulling the glass chamber out of the steel body's interior and cooling it rapidly after the process. It was an important benefit of being able to conduct the reaction in an entirely inert environment, the glass tube in the system.

Experiments were performed in the presence of water, ethyl acetate, acetone, and acetonitrile in water as co-solvents at different times. Cellulose is a polymer of glucose and depolymerisation of cellulose is possible by solvent handling. In our investigation, we looked into the co-solvent effect in depolymerization. The effect of solubility parameters on saccharification was also investigated.

Three trials were conducted to provide the most accurate findings. The liquid-solid product in the reactor glass chamber was filtered for separation purposes. The liquid part was analyzed by HPLC to define the quantity of sugar and organic acid. FTIR and TOC-SSM analysis were applied to the solid part after washing and drying. According to these results, structural changes were determined by analyzing certain band ranges in the spectra of the FTIR analysis of the solid structure. In addition, conversion calculations were made according to the starting quantity of solid matter and the amount of post-treatment solid matter. In addition, sugar types, sugar conversion ratio, and organic acid types formed over the carbon amount in the feed were calculated as percentage conversion.

Figure 4.2.2.1 Filtration of solid and liquid products

4.2.3 Analytical Methods

Different liquid and solid products were measured by using the relevant equipment.

4.2.3.1 High Performance Liquid Chromatography (HPLC)

One among the most well-known equipment used for analytical separation procedures is High Performance Liquid Chromatography (HPLC-Agilent), which is shown in Figure 4.2.3.1.1

Due to its adaptability, HPLC is utilized in a variety of commercial and academic domains, including forensics, environmental analysis, and the analysis of chemicals, medicines, and the environment.

In our investigation, HPLC was utilized to quantify the ppm quantities of sugars and organic acids generated in liquid products.

Figure 4.2.3.1.1 High Performance Liquid Chromatography

In an HPLC apparatus, the detector, column, pump, and degasser are the most crucial components.

The degasser unit is responsible for removing dissolved gas bubbles from the mobile phase reservoir or injection.

Pump causes mobile phase to be drawn from the reservoir and sample from the needle injection port, enabling it to traverse throughout the column. This is achieved by modifying the system's flow rate and pressure. Pumps can be gradient or isocratic. In isocratic elution, the solvent type and content do not vary throughout separation. in gradient elution, two to four dissimilarly polarized liquids are mixed together while being measured.

A column segregates the components based on their chemical and physical qualities. It has a stationary phase within, such as polymeric resins or silica. The several types of HPLC columns comprise the ion exchange, size exclusion, reverse phase, and normal phase.

Injection samplers come in two varieties: automatic and manual. With the manual type, a syringe and valve are utilized to inject the sample. When set to automatic, the gadget completes the task by itself. Nowadays, the majority of HPLCs are completely automated and computer controlled. In our instance, samples were manually injected into the HPLC for analysis.

Detectors identify the solute's constituents. HPLC detectors include UV-VIS detectors, Refractive index detectors, and mass spectrometers with evaporative light scattering detectors.

Table 4.2.3.1.1 provides information on the method employed as well as the characteristics of the HPLC apparatus used to analyze sugars and organic acids.

Table 4.2.3.1.1 HPLC characteristics and operational conditions for the procedure

Device	HPLC-RI (Agilent 1200A)
Column	HPX-87H column
Mobile Phase	5 mM H_2SO_4
Flowrate	0.6 mL/min
Detector	Refractive Index
Colon Temperature	30°C
Detector Temperature	30°C
Injected Volume	20 µL
Analysis Time	50 min

Figure 4.2.3.1.2 displays an illustration of an HPLC chromatogram in which the quantity of products produced can be observed from the given peaks.

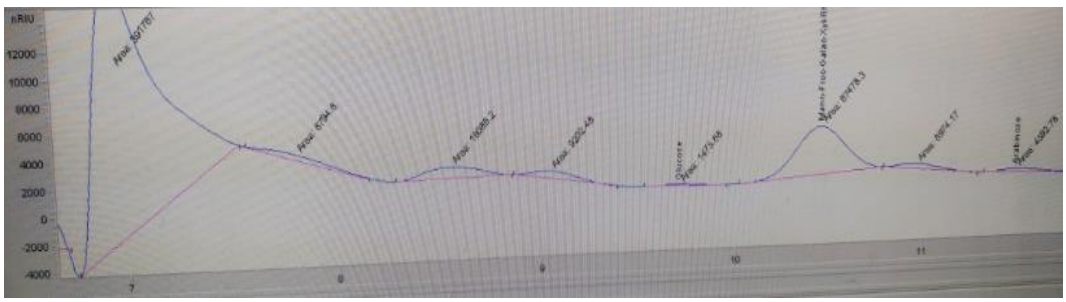

Figure 4.2.3.1.2 Example of HPLC chromatogram

4.2.3.2 Total organic carbon (TOC)

A TOC analyzer was utilized to calculate the total organic carbon amount in a liquid phase sample (Shimadzu total organic carbon analyzer-Model: TOC-VCPH). The gadget immediately calculates TOC according to the discrepancy between total carbon (TC) and inorganic carbon (IC). Two combustion tubes are used in the apparatus. They are, respectively, for total carbon and inorganic carbon. The liquid product is immediately combusted over tri-cobalt tetraoxide and platinum-based catalysts in a total carbon combustion tube. A liquid product is wet-oxidized in an IC combustion tube utilizing platinum-based catalysts and an H_3PO_4 solution applied to the surface of tricobalt tetraoxide. As a carrier gas, very pure air is employed. The measurement of CO_2 is done using a non-dispersive infrared detector since it happens in the combustion tubes (NDIR).

Table 4.2.3.2.1 Shimadzu TOC VCPH analytical conditions

Device	**TOC-VCPH.**
Measured items	TC, IC, TOC
Operation method	PC-controlled
Applicable samples	Aqueous sample
Measurement range (mg/L)	TC: 0 to 3500 / IC: 0 to 3500
Sample injection	Automatic injection
Automatic dilution	Dilution factor 2 to 50

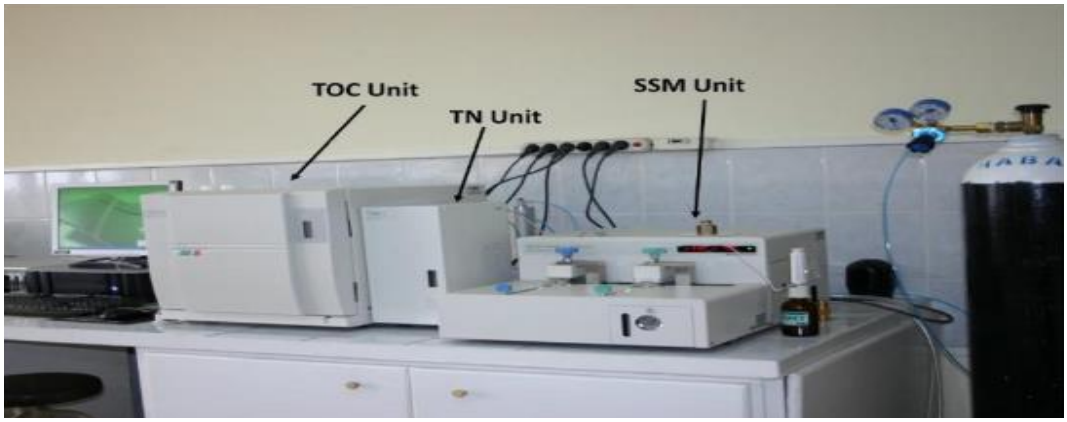

Figure 4.2.3.2.1 TOC device

4.2.3.3 SSM (Solid sample module)

Shimadzu TOC-SSM 5000A was used to quantify the total organic carbon in the solid sample (TOC). (Fig. 4.2.3.2.1)

Through the use of filter paper, solid residues were extracted from the aqueous solution. Following that, the solids were oven dried for 24 hours at 100 °C. After that, TOC-SSM analysis was used. As a consequence, conversion calculations were performed using the initial and post-treatment solid matter amounts.

4.2.3.4 FTIR (Fourier Transform Infrared Spectroscopy)

FTIR analysis was used as the major technique of assessment for the biomass sample, and the entire band range of spectral analysis was performed. Following filtering, washing, and drying procedures, the solid post-treatment residue was also examined by FTIR. The acquired FTIR spectra were carefully evaluated in terms of the qualitative interaction between lignin, cellulose, and hemicellulose for certain band values (figure 4.2.3.4.1).

Figure 4.2.3.4.1 FTIR (Fourier Transform Infrared Spectroscopy)

5. RESULTS

In this project, saccharification of almond shell by chemical pre-treatment using different solvents and co-solvents like water and a mixture of water-ethyl acetate, water-acetone, and water-acetonitrile was performed with a batch reactor setup. The alterations in the solid structure of biomass caused by solvents and the conversion to sugar were studied. Experiments were conducted under the conditions described in the thesis's prior section. The changes made were observed with solid and liquid devices (HPLC, TOC, TOC-SSM). The information gathered showed that the yield of solids and liquids differs varies according on the type of solvent and different times.

In addition, both the biomass sample and the post-treatment solid residues were evaluated by FTIR analysis and the rate of degradation of degradation of cellulose was observed.

Results are displayed as follows:

5.1 HPLC Results

Table 5.1.1 Variation of total sugars and organic acids yields due to chemical pre-treatment of almond shells in the presence of co-solvents such as water and a mixture of water-ethyl acetate, water-acetone, and water-acetonitrile at a ratio of 1: 1 with a water (solvent) / solid ratio of 2g solid / 18 mL solvent at 180 °C and different times

	Water			(Water: Acetone) (1:1 volumetric ratio)			(Water: Ethyl Acetate) (1: 1 volumetric ratio)			(Water: Acetonitrile) (1: 1 volumetric ratio)		
	20 min	40 min	60 min	20 min	40 min	60 min	20 min	40 min	60 min	20 min	40 min	60 min
cellobiose	0.90	0.46	0.28	2.68	8.28	8.39	13.58	1.11	0.17	16.37	16.44	16.03
Sucrose	0.11	0.14	0.07	0	0.11	0.18	0.26	0.33	0.06	0.11	0.09	0.12
Glucose	0.05	0.06	0.08	0	0.04	0.03	0.08	0.07	0.13	0.04	0.04	0.06
Mannose+ Fructose+ Galactose +Xylose+ Rhamnose	1.37	2.24	3.41	0.16	0.92	1.19	2.17	3.68	2.27	0.25	0.28	1.10
Arabinose	0.22	0	0.04	0.04	0.08	0.05	0.19	0.04	0.05	0.05	0.05	0.11
Total sugars %	**2.66**	**2.91**	**3.90**	**2.89**	**9.45**	**9.87**	**16.28**	**5.24**	**2.70**	**16.83**	**16.92**	**17.44**
Formic Acid	0.53	0.24	0.42	0.09	0.05	0.12	0.09	0.15	0.23	0	0.16	0.15
Acetic Acid	2.53	2.94	3.24	0.51	0.86	1.12	21.03	22.76	30.92	4.15	0.19	2.45
Levulinic Acid	0	0	0	0	0	0	0	0	0	0	1.90	0
5HMF	0	0	0	0	0	0	0	0	0	4.41	0.63	0
Total organic acids %	**3.12**	**3.18**	**3.66**	**0.60**	**0.92**	**1.25**	**21.13**	**22.91**	**31.16**	**8.57**	**2.90**	**2.61**
% CLE	**5,78**	**6.10**	**7.57**	**3.50**	**10.38**	**11.13**	**37,42**	**28.16**	**33.86**	**25.41**	**19.82**	**20.05**

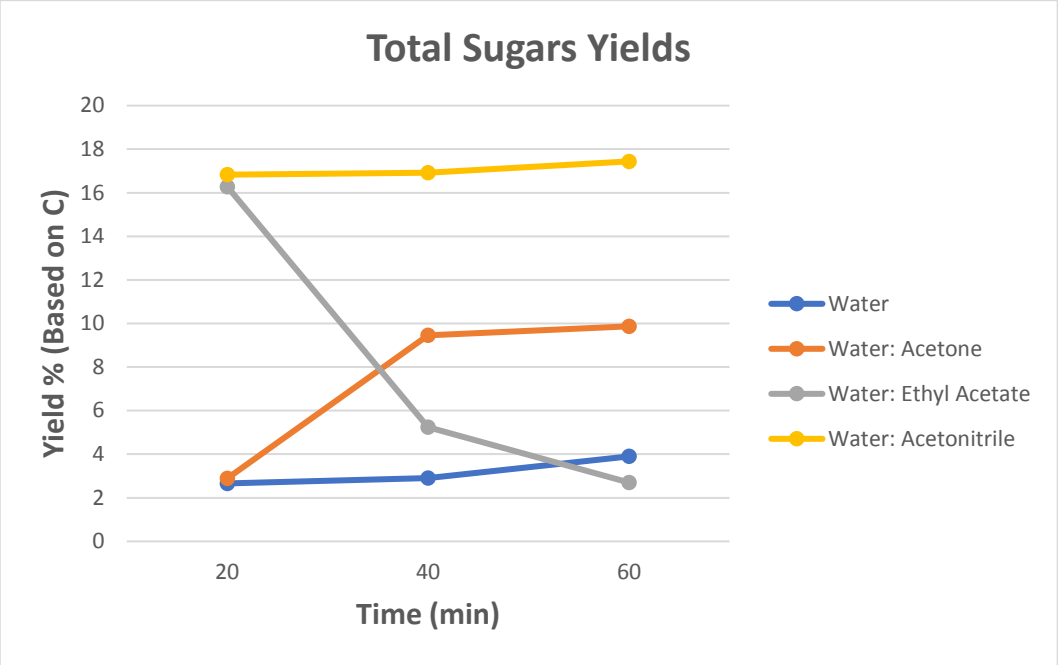

Figure 5.1.1 Variation of total sugars yield in the presence of co-solvents at 180 °C and three different time

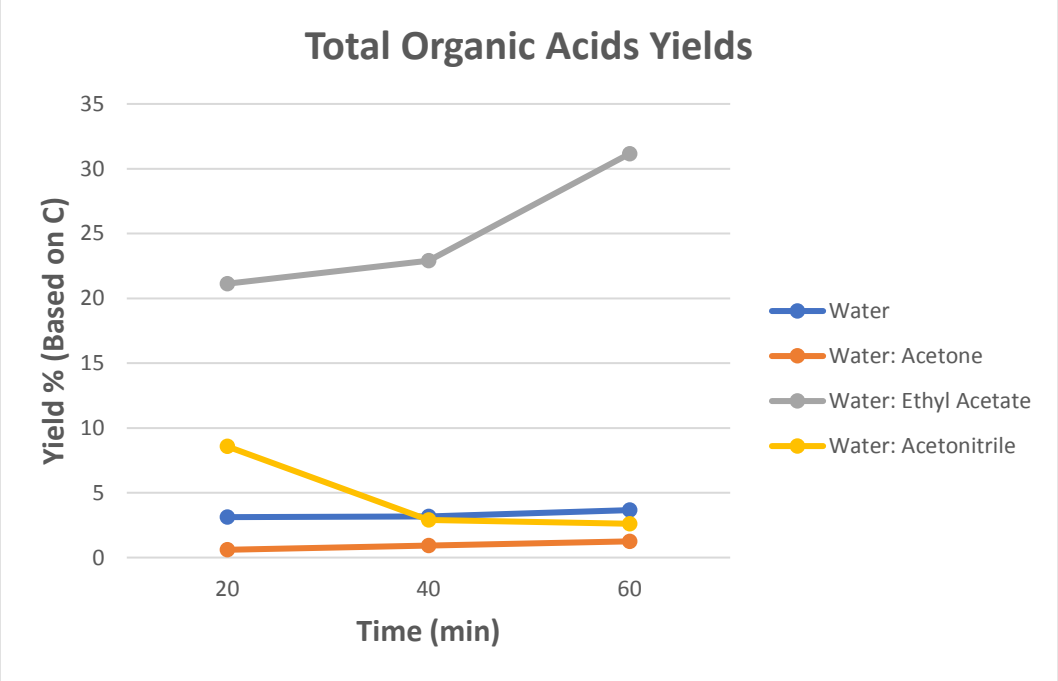

Figure 5.1.2 Variation of total organic acids yield in the presence of co-solvents at 180 °C and three different time

Figure 5.1.1 and Figure 5.1.2 show total sugars and organic acid yields produced due to chemical pre-treatment of almond shells at three different times. These graphics have been analyzed according to the ratio of the organic carbon of the product to the organic carbon of the feed.

The reaction temperature and biomass/solvent ratio were maintained constant in these tests at 180 °C and 2 g/18 ml, respectively. As co-solvents, we used water and a mixture of water-ethyl acetate, water-acetone, and water-acetonitrile at a 1: 1 ratio with water.

Three different research projects were conducted under the exact identical experimental settings. The findings, which were derived averaging the findings from this research are displayed in Table 5.1.

The greatest yield value for the total sugars produced by the solubilization and depolymerization of cellulose was reached at 60 minutes for water, a combination of water-acetone, and water-acetonitrile. As a result, they tended to grow over time. In contrast to these solvents, water-ethyl acetate tended to diminish over time.

The highest yield value in total organic acids generated by the procedure was achieved at 60 minutes for water, a combination of water-acetone and water-ethyl acetate. As a result, they tended to increase over time. Water-acetonitrile, in contrast to these solvents, tended to degrade with time.

By comparing the yields of different produced sugars, it is clear that water: acetonitrile shows the highest production efficiency in all three times among solvents.

And by comparing the yields of different produced organic acids, it is clear that Water: ethyl Acetate shows the highest production efficiency in all three times among solvents.

When the solvent was water: acetonitrile, total sugars reached a maximum of 17.44 at 60 minutes, and total organic acids yielded a maximum of 31.16 at 60 minutes in the presence of water: ethyl acetate.

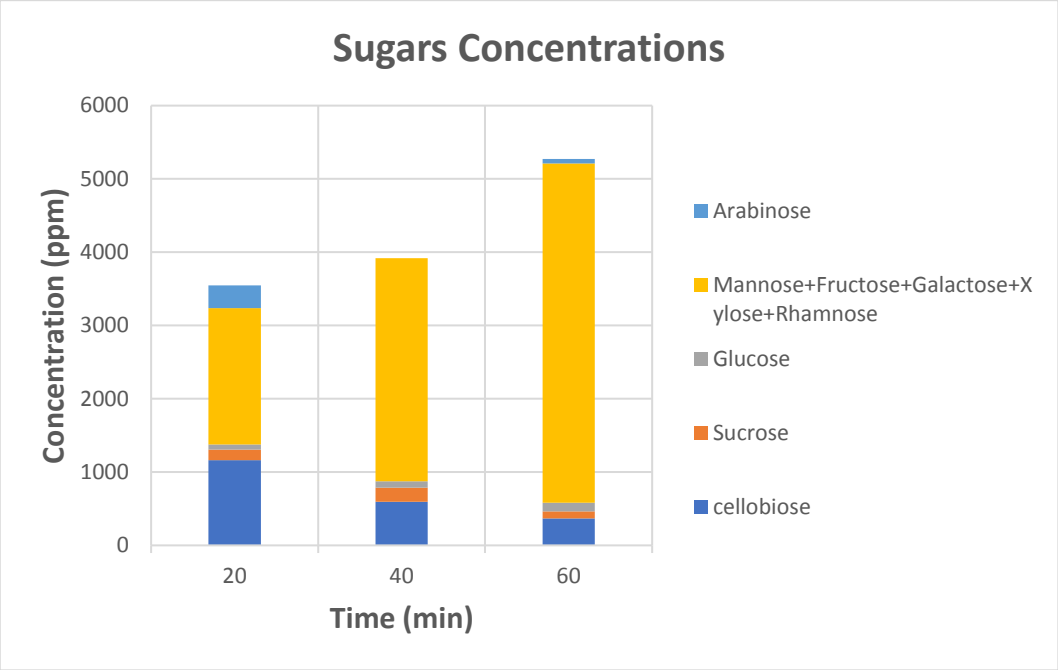

Figure 5.1.3 The concentration of different sugars produced due to chemical pre-treatment of almond shells in the presence of Water at 180 °C, and three different times

This figure shows the concentration of different sugars as ppm produced in the presence of water and a constant temperature of 180 °C for three specific times: 20, 40, and 60 minutes.

In fact, here, the concentration of individual sugars produced at 3 specific times is compared, and the highest amount of sugar produced is observed.

As mentioned above, results were achieved by averaging three repeated experiments that were carried out in exactly identical experimental settings.

Based on the illustration, with passing time, total sugar concentrations rose.

For all three times, the greatest concentration of sugars produced by the solubilization of cellulose was the sum of five sugars such as mannose, fructose, galactose, xylose, and rhamnose, which were observed at the individual peak of the HPLC device.

They account for about 1860 ppm for the time 20; 3041 ppm for the time 40; and 4627 ppm for the time 60.

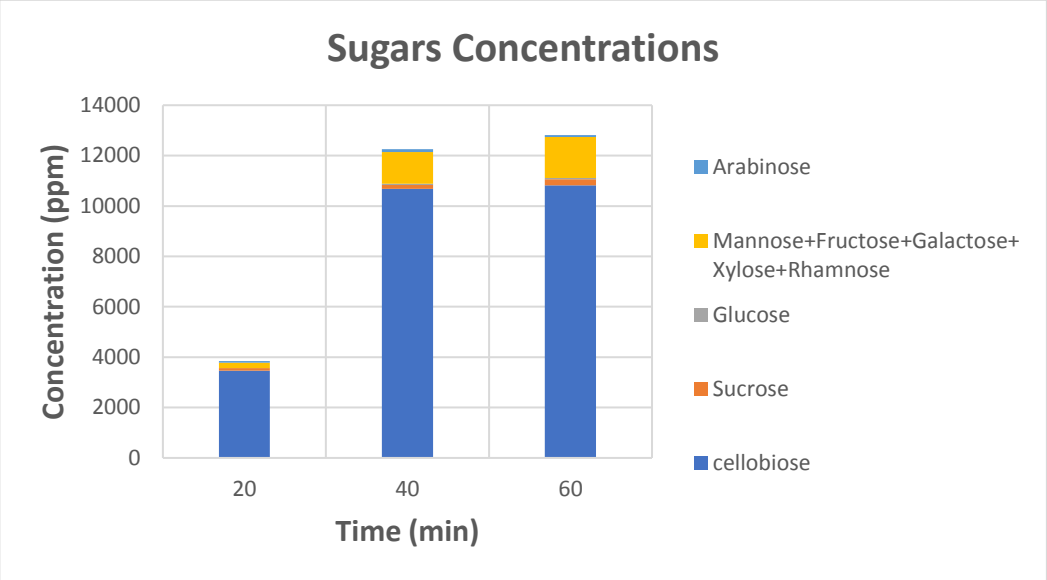

Figure 5.1.4 The concentration of different sugars produced due to chemical pre-treatment of almond shells in the presence of Water: Aceton at 180 °C, and three different times

This figure shows the concentration of different sugars as ppm produced in the presence of water, acetone, and a constant temperature of 180 °C for three specific times: 20, 40, and 60 minutes.

According to the illustration, total sugar concentrations increased with time.

For all three times, the greatest concentration of sugars produced by the solubilization of cellulose was the cellobiose, which was observed at the individual peak of the HPLC device.

It accounts for about 3462 ppm for the time 20, 10675 ppm for the time 40, and 10823 ppm for the time 60.

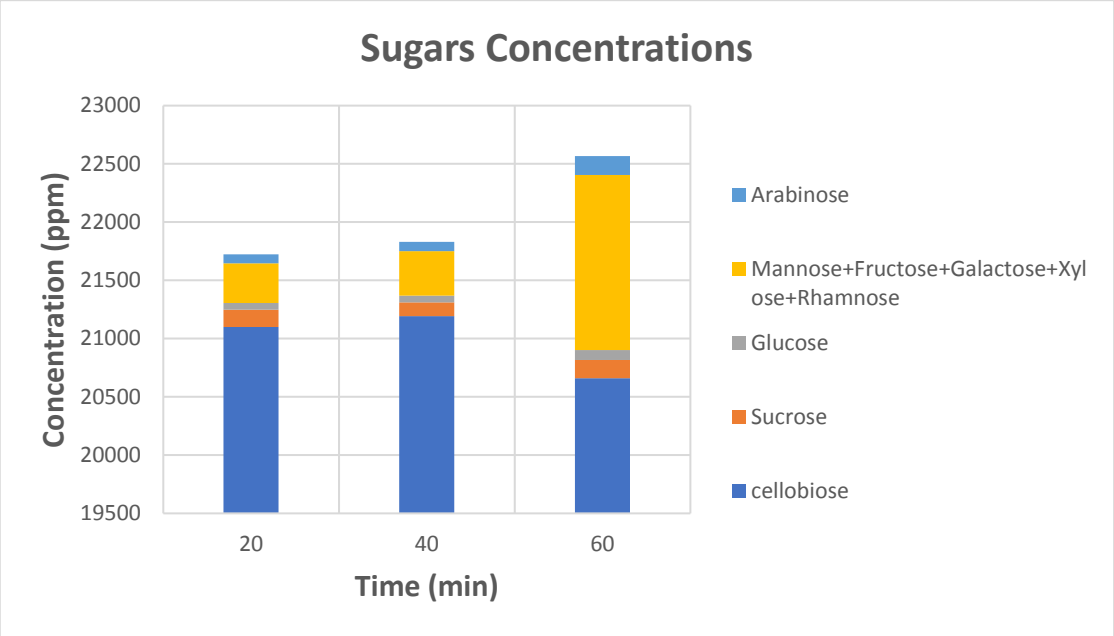

Figure 5.1.5 The concentration of different sugars produced due to chemical pre-treatment of almond shells in the presence of Water: Acetonitrile at 180 °C, and three different times

This figure shows the concentration of different sugars as ppm produced in the presence of water, acetonitrile, and a constant temperature of 180 °C for three specific times: 20, 40, and 60 minutes.

As seen in the graphic, total sugar concentrations increased as time passed.

For all three times, the greatest concentration of sugars produced by the solubilization of cellulose was the cellobiose, which was observed at the individual peak of the HPLC device.

It accounts for about 21100 ppm for the time 20; 21194 ppm for the time 40; and 20660 ppm for the time 60.

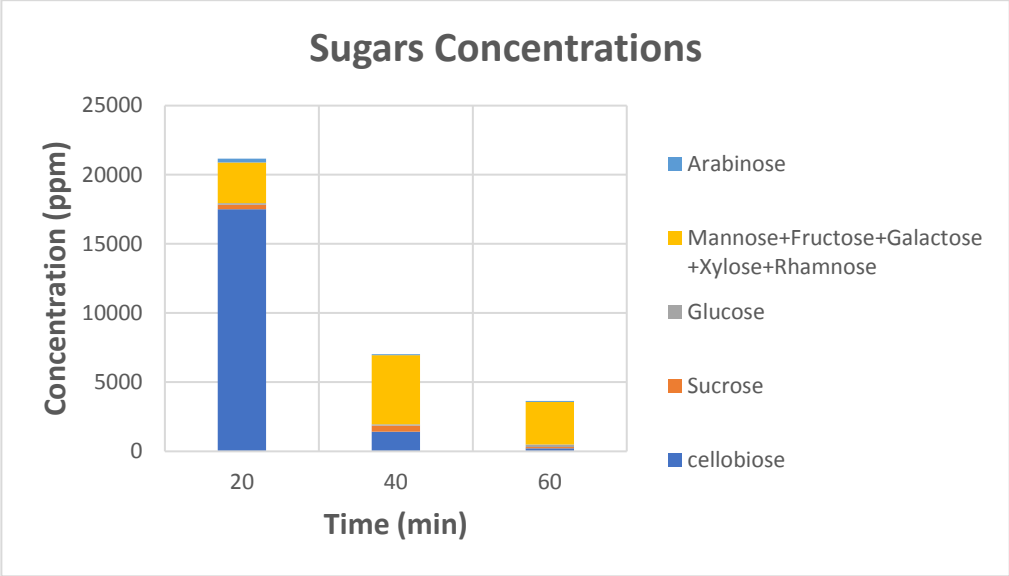

Figure 5.1.6 The concentration of different sugars produced due to chemical pre-treatment of almond shells in the presence of Water: Ethyl Acetate at 180 °C, and three different times

This figure shows the concentration of different sugars as ppm produced in the presence of water, ethyl acetate, and a constant temperature of 180 °C for three specific times: 20, 40, and 60 minutes.

As the illustration indicates, total sugar concentrations decreased as time passed.

At time 20, the greatest concentration of sugar produced by the solubilization of cellulose was cellobiose, which was observed at the individual peak of the HPLC device. It accounts for about 17500 ppm.

For time 40, the greatest concentration of sugar produced by the solubilization of cellulose was the sum of five sugars such as mannose, fructose, galactose, xylose, and rhamnose, which were observed at the individual peak of the HPLC device. They account for about 4998 ppm.

For time 60, the greatest concentration of sugar produced by the solubilization of cellulose was the sum of five sugars such as mannose, fructose, galactose, xylose, and rhamnose, which were observed at the individual peak of the HPLC device. They account for about 3081 ppm.

5.2 FTIR Results

FTIR spectroscopy was applied to properly evaluate the almond shell and also solid remnants. Based on comparable cellulose values, the distinctive wave numbers for cellulose decomposition were detected.

Aside from the FTIR spectra values supplied, the complete FTIR band for each sample was analyzed to describe the dissolving impacts of solvent and co-solvent systems. Thus, structural alterations were noticed.

The literature indicates that the distinctive cellulose absorption peaks appear at ῡ=1374, 1328, 1163, 1056 and 898 cm $^{-1}$. And band at ῡ=898 cm $^{-1}$ depicts cellulose's crystalline structure.

In addition, the peak at 3200-3331 cm $^{-1}$ includes inter- and intra-molecular hydrogen bond vibrations in cellulose.

The figure below shows the FTIR bond for almond shell as our raw material.

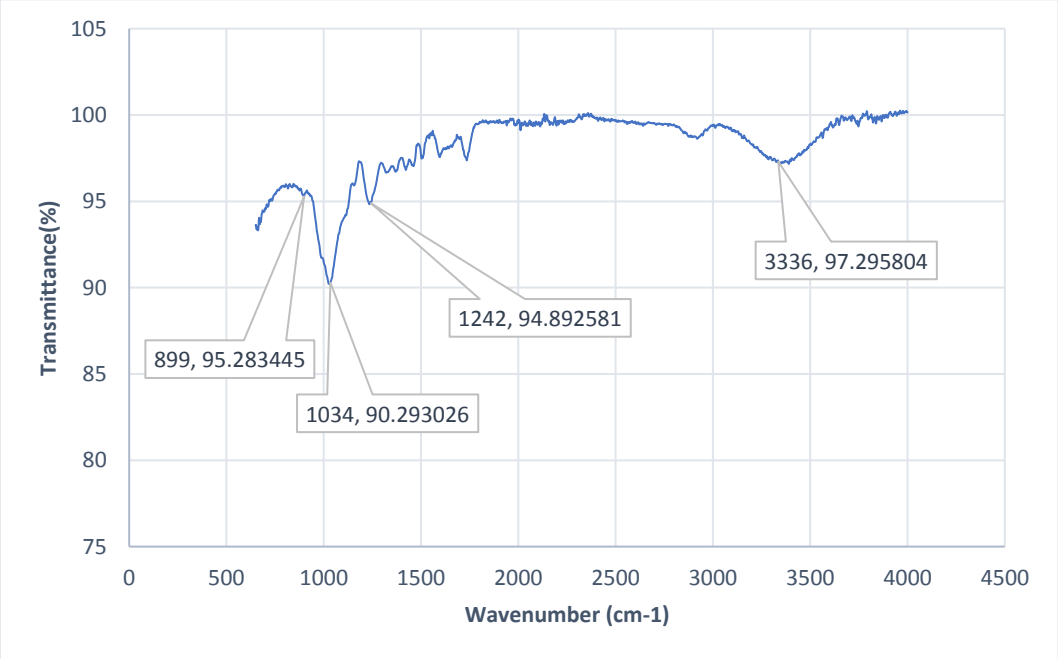

Figure 5.2.1 FTIR spectra of almond shells

5.2.1 Evaluation of FTIR Spectra of Solid Residues from Almond Shells Pretreatment with Water at 3 Different Times Compared to FTIR Spectra of Almond Shells

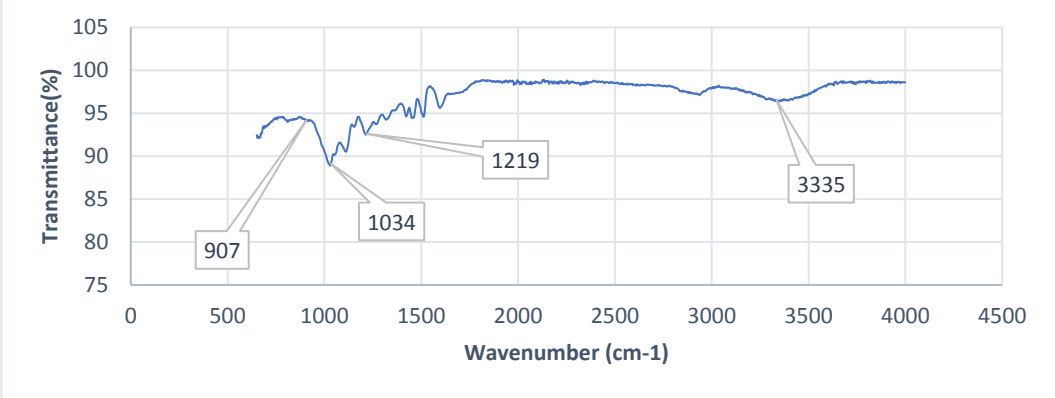

Figure 5.2.1.1 FTIR spectra of solid residue at the 20th minute in the presence of water

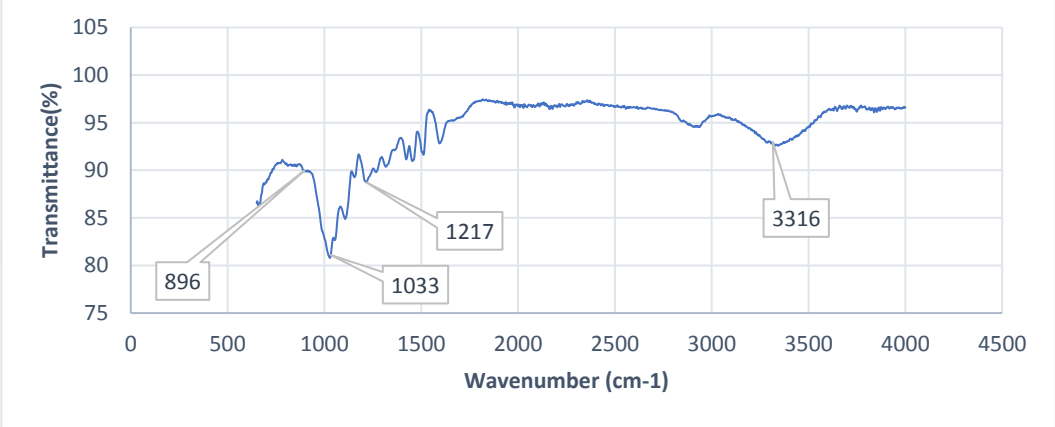

Figure 5.2.1.2 FTIR spectra of solid residue at the 40th minute in the presence of water

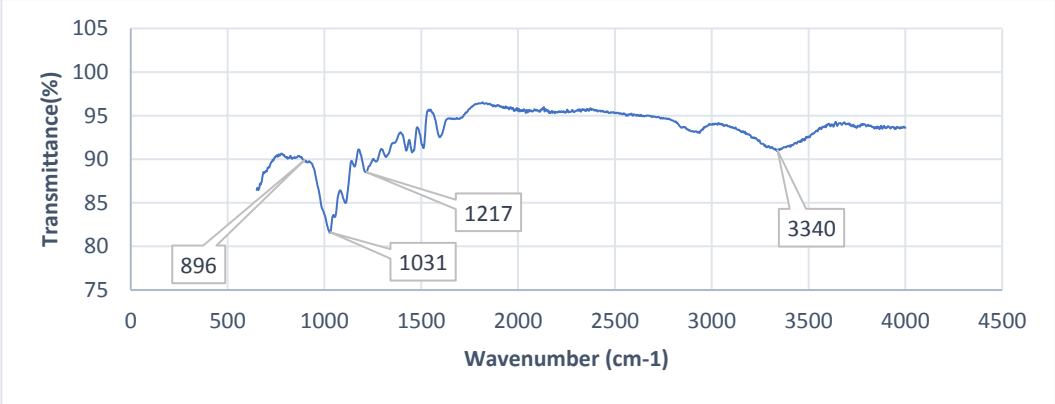

Figure 5.2.1.3 FTIR spectra of solid residue at the 60th minute in the presence of water

Figure 5.2.1.1, Figure 5.2.1.2, and Figure 5.2.1.3 show FTIR spectra of solid residues of almond shells pretreated with Water at three different times of 20, 40, and 60 minutes, respectively. As seen in the figures, the most changes occur when the time is 60.

By comparing the FTIR spectra of solid residue at all three times with the raw biomass almond shell, we come to the conclusion that the absorption peaks of cellulose in the range of (1034 cm^{-1} and 1219 cm^{-1}) for twentieth minute, (1033 cm^{-1} and 1217 cm^{-1}) for fortieth minute and (1031 cm^{-1} and 1217 cm^{-1}) for sixtieth minute decreased gradually at all three times. The decreasing of these peaks shows that at this stage in the experiment, the cellulose in the almond shell had been transformed.

The band at $\breve{\upsilon}$=896 cm^{-1} and $\breve{\upsilon}$=907 cm^{-1} which depict the crystalline structure of cellulose, vanished as time passed, supporting the assumption that crystalline cellulose was likewise transformed.

The band at 3335 cm^{-1}, 3316 cm^{-1} and 3340 cm^{-1} which represent the inter- and intra-molecular hydrogen bond vibrations in cellulose, decreased at all three times. The fact that this peak has decreased shows that water molecules may have had a significant interaction with the end-OH group of the glucose unit, which led to an increase in the breakdown of both inter- and intramolecular hydrogen bonds.

5.2.2 Evaluation of FTIR Spectra of Solid Residues from Almond Shells Pretreatment with Water: Acetone at 3 Different Times Compared to FTIR Spectra of Almond Shells

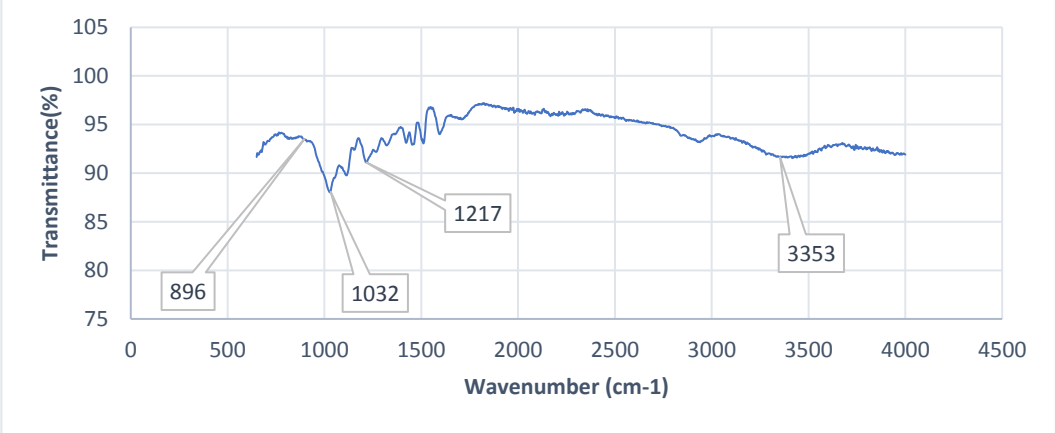

Figure 5.2.2.1 FTIR spectra of solid residue at the 20th minute in the presence of Water: Acetone

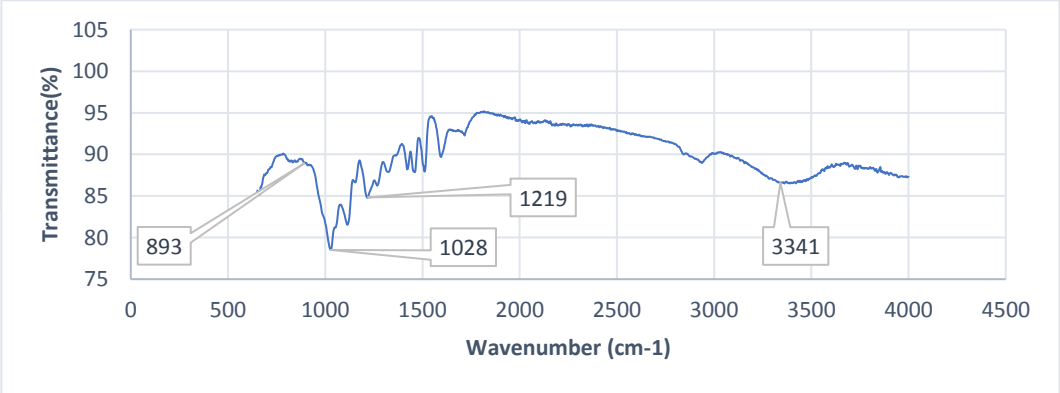

Figure 5.2.2.2 FTIR spectra of solid residue at the 40th minute in the presence of Water: Acetone

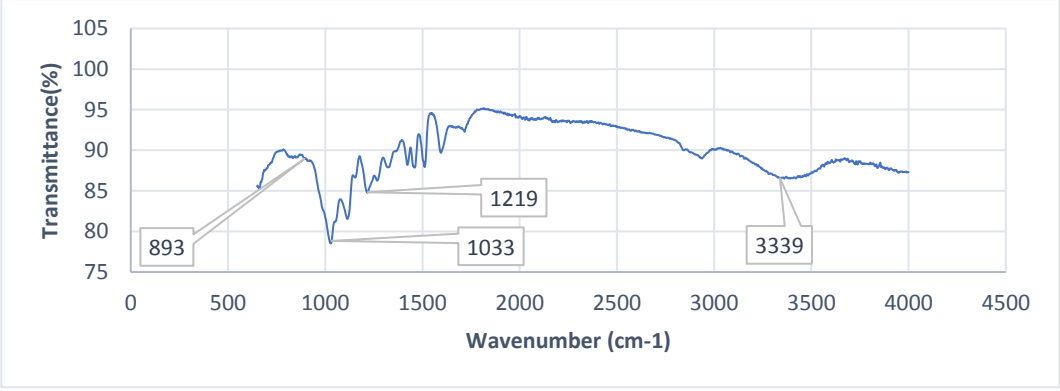

Figure 5.2.2.3 FTIR spectra of solid residue at the 60th minute in the presence of Water: Acetone

Figure 5.2.2.1, Figure 5.2.2.2, and Figure 5.2.2.3 show FTIR spectra of solid residues of almond shells pretreated with Water: Aceton at three different times, 20, 40, and 60 minutes, respectively. As seen in the figures, the most changes occur at the times of 40 and 60 minutes.

By comparing the FTIR spectra of solid residue at all three times with the raw biomass almond shell, we come to the conclusion that the absorption peaks of cellulose in the range of (1032 cm^{-1} and 1217 cm^{-1}) for twentieth minute, (1028 cm^{-1} and 1219 cm^{-1}) for fortieth minute and (1033 cm^{-1} and 1219 cm^{-1}) for sixtieth minute decreased gradually at all three times. The decreasing of these peaks shows that at these stages in the experiment, the cellulose in the almond shell had been transformed.

The band at $\breve{\upsilon}$=893 cm^{-1} and $\breve{\upsilon}$=896 cm^{-1} which depict the crystalline structure of cellulose, vanished as time passed, supporting the assumption that crystalline cellulose was likewise transformed.

The band at 3353 cm^{-1}, 3341 cm^{-1} and 3339 cm^{-1} which represent the inter- and intra-molecular hydrogen bond vibrations in cellulose, decreased at all three times.

5.2.3 Evaluation of FTIR Spectra of Solid Residues from Almond Shells Pretreatment with Water: Ethyl Acetate at 3 Different Times Compared to FTIR Spectra of Almond Shells

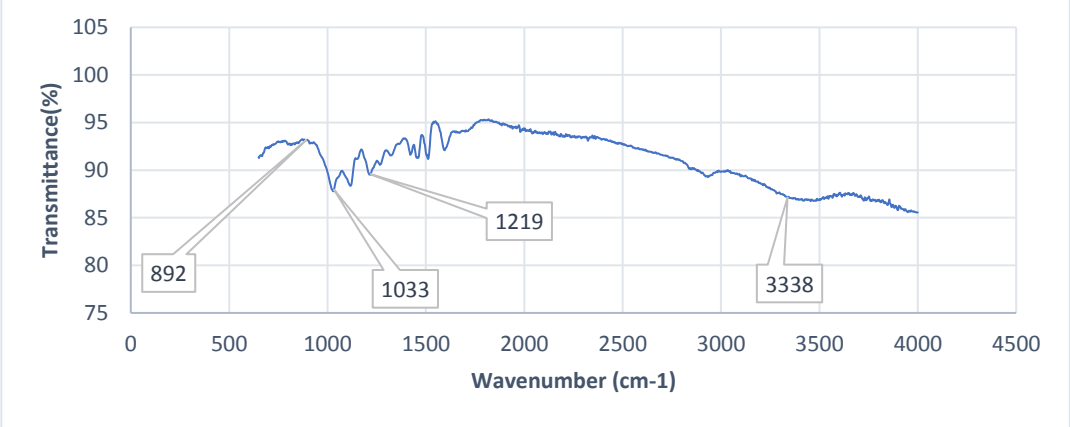

Figure 5.2.3.1 FTIR spectra of solid residue at the 20th minute in the presence of Water: Ethyl Acetate

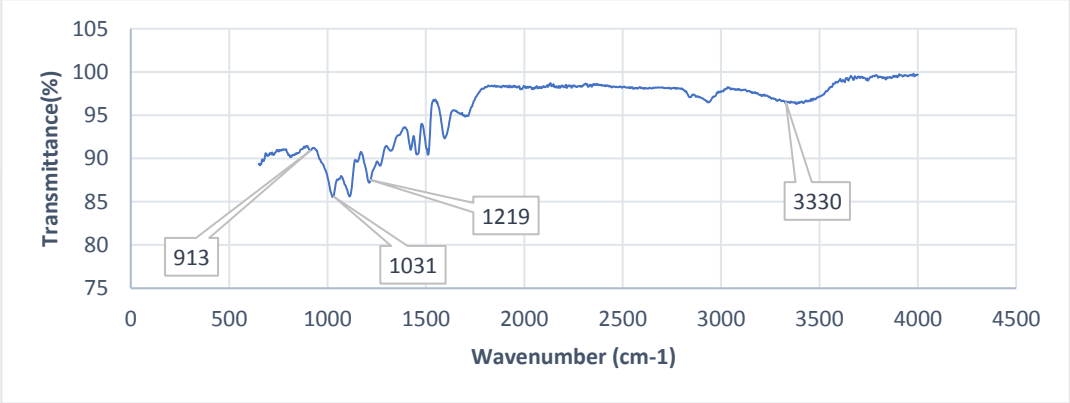

Figure 5.2.3.2 FTIR spectra of solid residue at the 40th minute in the presence of Water: Ethyl Acetate

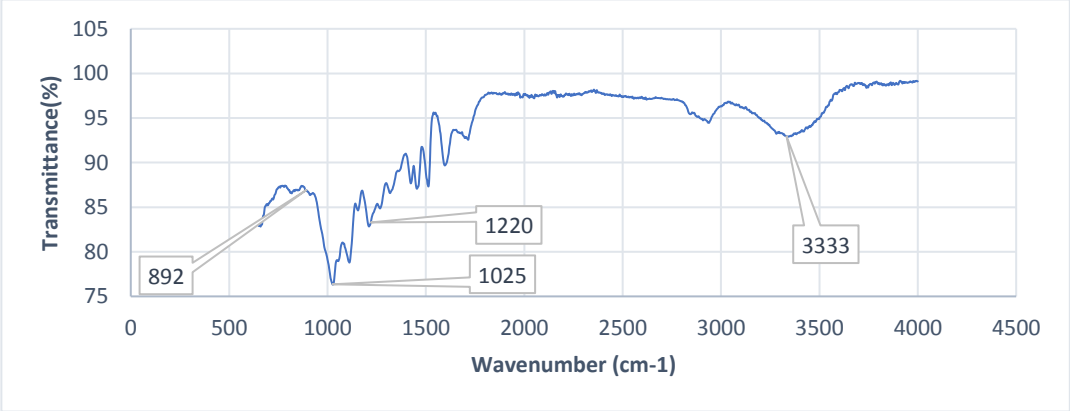

Figure 5.2.3.3 FTIR spectra of solid residue at the 60th minute in the presence of Water: Ethyl Acetate

Figure 5.2.3.1, Figure 5.2.3.2, and Figure 5.2.3.3 show FTIR spectra of solid residues of almond shells pretreated with Water: Ethyl Acetate at three different times, 20, 40, and 60 minutes, respectively. As seen in the figures, the most changes occur when the time is 60.

By comparing the FTIR spectra of solid residue at all three times with the raw biomass almond shell, we come to the conclusion that the absorption peaks of cellulose in the range of (1033 cm^{-1} and 1219 cm^{-1}) for twentieth minute, (1031 cm^{-1} and 1219 cm^{-1}) for fortieth minute and (1025 cm^{-1} and 1220 cm^{-1}) for sixtieth minute decreased gradually at all three times. The decreasing of these peaks shows that at this stage in the experiment, the cellulose in the almond shell had been transformed.

The band at $\breve{\upsilon}$=889 cm^{-1} and $\breve{\upsilon}$=913 cm^{-1} which depicts the crystalline structure of cellulose, vanished as time passed, supporting the assumption that crystalline cellulose was likewise transformed.

The band at 3338 cm^{-1}, 3330 cm^{-1} and 3333 cm^{-1} which represent the inter- and intra-molecular hydrogen bond vibrations in cellulose, decreased significantly at the twentieth and fortieth minutes.

5.2.4 Evaluation of FTIR Spectra of Solid Residues from Almond Shells Pretreatment with Water: Acetonitrile at 3 Different Times Compared to FTIR Spectra of Almond Shells

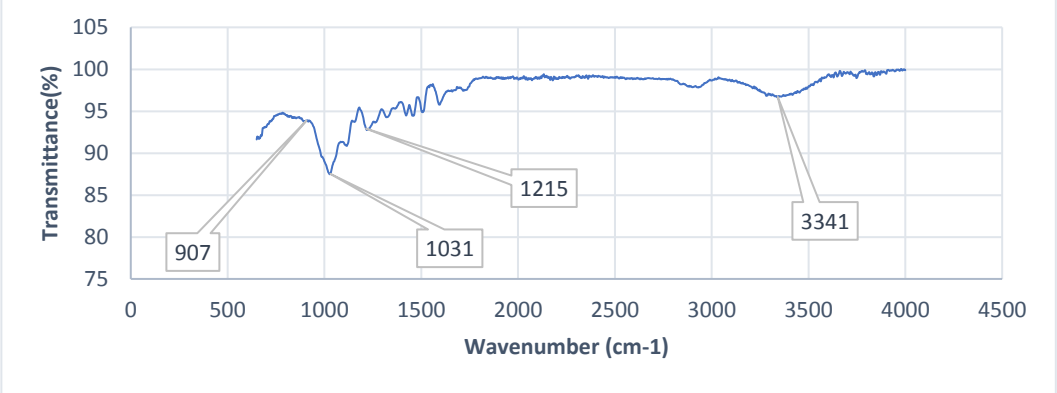

Figure 5.2.4.1 FTIR spectra of solid residue at the 20th minute in the presence of Water: Acetonitrile

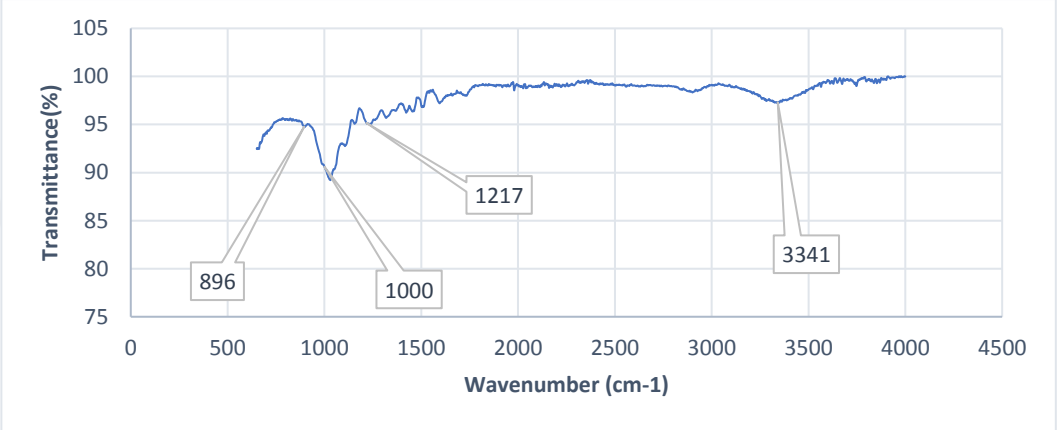

Figure 5.2.4.2 FTIR spectra of solid residue at the 40th minute in the presence of Water: acetonitrile

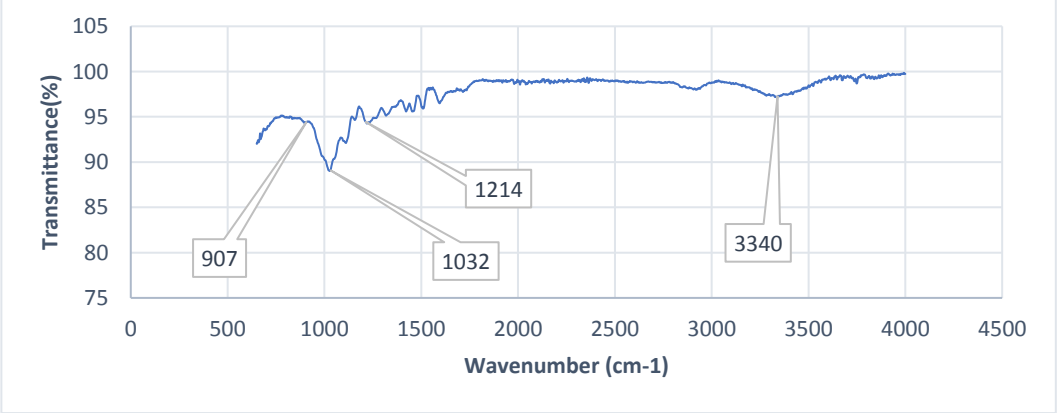

Figure 5.2.4.3 FTIR spectra of solid residue at the 60th minute in the presence of Water: Acetonitrile

Figure 5.2.4.1, Figure 5.2.4.2, and Figure 5.2.4.3 show FTIR spectra of solid residues of almond shells pretreated with Water: Acetonitrile at three different times, 20, 40, and 60 minutes, respectively.

By comparing the FTIR spectra of solid residue at all three times with the raw biomass almond shell, we come to the conclusion that the absorption peaks of cellulose in the range of (1031 cm^{-1} and 1215 cm^{-1}) for twentieth minute, (1000 cm^{-1} and 1217 cm^{-1}) for fortieth minute and (1032 cm^{-1} and 1214 cm^{-1}) for sixtieth minute decreased gradually at all three times. The decreasing of these peaks shows that at this stage in the experiment, the cellulose in the almond shell had been transformed.

The band at $\breve{\upsilon}$=896 cm^{-1} and $\breve{\upsilon}$=907 cm^{-1} which depicts the crystalline structure of cellulose, vanished as time passed, supporting the assumption that crystalline cellulose was likewise transformed.

The band at 3341 cm^{-1} and 3340 cm^{-1} which represents the inter- and intra-molecular hydrogen bond vibrations in cellulose, decreased with the time increasing.

6.0 CONCLUSION

Chemical pre-treatment of almond shell as a real biomass feedstock with different solvents and co-solvents like water and a mixture of water-ethyl acetate, water-acetone, and water-acetonitrile was conducted successfully in a batch reactor system.

This experimental study looked at the alterations in the solid structure of biomass caused by different solvents as well as the solubilization of almond shell for high yields of saccharification.

Both the biomass sample and the post-treatment solid residues were evaluated by FTIR analysis and the rate of degradation of cellulose was observed. In addition, the liquid products were analyzed by using HPLC for sugars and organic acids formed in the experiments. And finally, TOC analyses were carried out for both liquid and solid samples.

In both total sugars and total organic acids, yield increased with rising time from 20 minutes to 60 minutes, except for two cases. The first is related to the treatment with Water: Ethyl Acetate, which tended to diminish the sugar amounts over time, and the second is related to the treatment with Water: Acetonitrile, which tended to degrade the organic acids with time.

Chemical pretreatment of almond shell with Water: Acetonitrile in 1:1 ratio showed the highest sugar production efficiency in all three times among solvents. We conclude that Water: Acetonitrile as a co-solvent could better solubilize the almond shells, resulting in more sugars among the other co-solvents.

An FTIR band for each sample was analyzed to describe the dissolving impacts of solvent and co-solvent systems compared with the FTIR spectra of almond shells. The band at 3334 cm^{-1} which represents the inter- and intra-molecular hydrogen bond vibrations in cellulose, decreased significantly in all solvents.

The decreasing of this peak indicates that solvent molecules had considerable contact with the end-OH group of the glucose unit, resulting in an increase in the breakdown of both inter- and intramolecular hydrogen bonds.

By comparing the FTIR spectra of solid residue with the raw biomass almond shell at all three times in all solvents, we come to the conclusion that the absorption peaks of cellulose in the range of 899, 1034 and 1219 cm^{-1} decreased gradually with increasing pretreatment time.

The high efficiency to be obtained from the conversion of the lignocellulosic structure to sugar in the platform chemical recovery will also make the conversion of this intermediate product into valuable chemicals in the catalytic environment efficient. Platform chemicals can be used both as raw materials and directly as additives in the chemical industry. In the production of various chemicals in the field of petrochemicals, especially important intermediates such as Levulinic Acid are an important intermediate that can be converted into other chemicals. In this context, large-scale studies can be planned with industrial organizations that care about the concept of biorefinery, which will be an alternative to classical fossil-based technologies operating in the field of energy in biomass-based technology development.

REFERENCE

Dwyer, S., & Teske, S. (2018). Renewables 2018 global status report. *Renewables 2018 Global Status Report*.

Perea-Moreno, M.-A., Samerón-Manzano, E., & Perea-Moreno, A.-J. (2019). Biomass as renewable energy: Worldwide research trends. *Sustainability, 11*(3), 863.

Nunes, L., Causer, T., & Ciolkosz, D. (2020). Biomass for energy: A review on supply chain management models. *Renewable and Sustainable Energy Reviews, 120*, 109658.

Pasangulapati, V., Ramachandriya, K. D., Kumar, A., Wilkins, M. R., Jones, C. L., & Huhnke, R. L. (2012). Effects of cellulose, hemicellulose and lignin on thermochemical conversion characteristics of the selected biomass. *Bioresource technology*, *114*, 663-669.

Dilip, H. N., & Chakraborty, D. (2019). Hydrophilicity of the hydrophobic group: Effect of cosolvents and ions. *Journal of Molecular Liquids*, *280*, 389-398.

Kalashnikova, I., Bizot, H., Cathala, B., & Capron, I. (2012). Modulation of cellulose nanocrystals amphiphilic properties to stabilize oil/water interface. *Biomacromolecules*, *13*(1), 267-275.

Bhatia, S. K., Jagtap, S. S., Bedekar, A. A., Bhatia, R. K., Patel, A. K., Pant, D., ... & Yang, Y. H. (2020). Recent developments in pretreatment technologies on lignocellulosic biomass: effect of key parameters, technological improvements, and challenges. *Bioresource technology*, *300*, 122724.

Michaelides, E. E. S. (2012). *Alternative energy sources*: Springer Science & Business Media.

Kumar, B., Bhardwaj, N., Agrawal, K., Chaturvedi, V., & Verma, P. (2020). Current perspective on pretreatment technologies using lignocellulosic biomass: An emerging biorefinery concept. *Fuel Processing Technology, 199*, 106244.

Statistics, W. G. B. (2019). World Bioenergy Association: Stockholm.

IEA. (2019). Statistics. Retrieved from https://www.iea.org/statistics/

Demirbaş, A. (2001). Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy conversion and Management, 42*(11), 1357-1378.

Güney, T., & Kantar, K. (2020). Biomass energy consumption and sustainable development. *International Journal of Sustainable Development & World Ecology*, *27*(8), 762-767.

Dalena, F., Basile, A., & Rossi, C. (2017). *Bioenergy systems for the future: prospects for biofuels and biohydrogen*: Woodhead Publishing.

Goldemberg, J., & Coelho, S. T. (2004). Renewable energy—traditional biomass vs. modern biomass. *Energy Policy*, *32*(6), 711-714.

REFERENCE (Conts.)

Ozturk, M., Saba, N., Altay, V., Iqbal, R., Hakeem, K. R., Jawaid, M., & Ibrahim, F. H. (2017). Biomass and bioenergy: An overview of the development potential in Turkey and Malaysia. *Renewable and Sustainable Energy Reviews*, *79*, 1285-1302.

Peterson, A. A., Vogel, F., Lachance, R. P., Fröling, M., Antal Jr, M. J., & Tester, J. W. (2008). Thermochemical biofuel production in hydrothermal media: a review of sub-and supercritical water technologies. *Energy & environmental science*, *1*(1), 32-65.

Lee, H. V., Hamid, S. B. A., & Zain, S. K. (2014). Conversion of lignocellulosic biomass to nanocellulose: structure and chemical process. *The Scientific World Journal*, *2014*.

Isikgor, F. H., & Becer, C. R. (2015). Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polymer Chemistry*, *6*(25), 4497-4559.

Chen, H. (2014). Chemical composition and structure of natural lignocellulose. In *Biotechnology of lignocellulose* (pp. 25-71). Springer, Dordrecht.

Mohan, D., Pittman Jr, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & fuels*, *20*(3), 848-889.

Roy, R., Rahman, M. S., & Raynie, D. E. (2020). Recent advances of greener pretreatment technologies of lignocellulose. *Current Research in Green and Sustainable Chemistry*, *3*, 100035.

Alaswad, A., Dassisti, M., Prescott, T., & Olabi, A. G. (2015). Technologies and developments of third generation biofuel production. *Renewable and Sustainable Energy Reviews*, *51*, 1446-1460.

Werkelin, J., Skrifvars, B. J., & Hupa, M. (2005). Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. *Biomass and Bioenergy*, *29*(6), 451-466.

Rowell, R.M., Pettersen, R., Tshabalala, A. M., 2012, Handbook of Wood Chemistry and Wood Composites

Brodeur, G., Yau, E., Badal, K., Collier, J., Ramachandran, K., & Ramakrishnan, S. (2011). Chemical and physicochemical pretreatment of lignocellulosic biomass: a review. *Enzyme research*, *2011*.

Lebaka, V. R. (2013). Potential bioresources as future sources of biofuels production: An Overview. *Biofuel technologies: Recent developments*, 223-258.

Nussbaumer, T. (2003). Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction. *Energy & fuels*, *17*(6), 1510-1521.

Kaushika, N., Reddy, K., & Kaushik, K. (2016). Biomass energy and power systems. In *Sustainable Energy and the Environment: A Clean Technology Approach* (pp. 121-137): Springer.

REFERENCE (Conts.)

Tursi, A. (2019). A review on biomass: importance, chemistry, classification, and conversion. *Biofuel Research Journal, 6*(2), 962-979.

Di Blasi, C. (2008). Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in energy and combustion science, 34*(1), 47-90.

Portha, J.-F., Parkhomenko, K., Kobl, K., Roger, A.-C., Arab, S., Commenge, J.-M., & Falk, L. (2017). Kinetics of methanol synthesis from carbon dioxide hydrogenation over copper–zinc oxide catalysts. *Industrial & Engineering Chemistry Research, 56*(45), 13133-13145.

Kaltschmitt, M. (2019). Renewable Energy from Biomass: Introduction. In *Energy from Organic Materials (Biomass)* (pp. 1-14): Springer.

Rahimpour, M., Aboosadi, Z. A., & Jahanmiri, A. (2012). Synthesis gas production in a novel hydrogen and oxygen perm-selective membranes tri-reformer for methanol production. *Journal of Natural Gas Science and Engineering, 9*, 149-159.

Molino, A., Chianese, S., & Musmarra, D. (2016). Biomass gasification technology: The state of the art overview. *Journal of Energy Chemistry, 25*(1), 10-25.

Akia, M., Yazdani, F., Motaee, E., Han, D., & Arandiyan, H. (2014). A review on conversion of biomass to biofuel by nanocatalysts. *Biofuel Research Journal, 1*(1), 16-25.

Yu, G., Zhang, Y., Schideman, L., Funk, T., & Wang, Z. (2011). Distributions of carbon and nitrogen in the products from hydrothermal liquefaction of low-lipid microalgae. *Energy & Environmental Science, 4*(11), 4587-4595.

McKendry, P. (2002). Energy production from biomass (part 2): conversion technologies. *Bioresource technology, 83*(1), 47-54.

Gollakota, A., Kishore, N., & Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews, 81*, 1378-1392.

Rowbotham, J., Dyer, P. W., Greenwell, H., & Theodorou, M. (2012). Thermochemical processing of macroalgae: a late bloomer in the development of third-generation biofuels? *Biofuels, 3*(4), 441-461.

Barreiro, D. L., Prins, W., Ronsse, F., & Brilman, W. (2013). Hydrothermal liquefaction (HTL) of microalgae for biofuel production: state of the art review and future prospects. *Biomass and bioenergy, 53*, 113-127.

Möller, M., Nilges, P., Harnisch, F., & Schröder, U. (2011). Subcritical water as reaction environment: fundamentals of hydrothermal biomass transformation. *ChemSusChem, 4*(5), 566-579.

Toor, S. S., Rosendahl, L., & Rudolf, A. (2011). Hydrothermal liquefaction of biomass: a review of subcritical water technologies. *Energy, 36*(5), 2328-2342.

REFERENCE (Conts.)

Gbashi, S., Adebo, O. A., Piater, L., Madala, N. E., & Njobeh, P. B. (2017). Subcritical water extraction of biological materials. *Separation & Purification Reviews, 46*(1), 21-34.

Cardenas-Toro, F. P., Alcazar-Alay, S. C., Forster-Carneiro, T., & Meireles, M. A. A. (2014). Obtaining oligo-and monosaccharides from agroindustrial and agricultural residues using hydrothermal treatments. *Food Public Health, 4*(3), 123-139.

Malaspina, D. C., & Faraudo, J. (2019). Molecular insight into the wetting behavior and amphiphilic character of cellulose nanocrystals. *Advances in Colloid and Interface Science, 267*, 15-25.

Jiang, Z., Yi, J., Li, J., He, T., & Hu, C. (2015). Promoting effect of sodium chloride on the solubilization and depolymerization of cellulose from raw biomass materials in water. *ChemSusChem, 8*(11), 1901-1907.

Cai, J., & Zhang, L. (2005). Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions. *Macromolecular bioscience, 5*(6), 539-548.

Hasegawa, I., Tabata, K., Okuma, O., & Mae, K. (2004). New Pretreatment Methods Combining a Hot Water Treatment and Water/Acetone Extraction for Thermo-Chemical Conversion of Biomass. *Energy & fuels, 18*(3), 755-760. doi:10.1021/ef030148e

Araque, E., Parra, C., Freer, J., Contreras, D., Rodríguez, J., Mendonça, R., & Baeza, J. (2008). Evaluation of organosolv pretreatment for the conversion of Pinus radiata D. Don to ethanol. *Enzyme and Microbial Technology, 43*(2), 214-219. doi:https://doi.org/10.1016/j.enzmictec.2007.08.006

Zhang, Y. H. P., Ding, S. Y., Mielenz, J. R., Cui, J. B., Elander, R. T., Laser, M., . . . Lynd, L. R. (2007). Fractionating recalcitrant lignocellulose at modest reaction conditions. *Biotechnology and bioengineering, 97*(2), 214-223.

Junnienkul, N., Sriariyanun, M., Douzou, T., Yasurin, P., & Asavasanti, S. (2018). Optimization of alkyl imidazolium chloride pretreatment on rice straw biomass conversion. *Applied Science and Engineering Progress, 11*(3), 199-207.

Lin, X., Jiang, K., Liu, X., Han, D., & Zhang, Q. (2022). Review on development of ionic liquids in lignocellulosic biomass refining. *Journal of Molecular Liquids, 359*, 119326. doi:https://doi.org/10.1016/j.molliq.2022.119326

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RESUME

Sanaz SAMADI ZENOUZ received her BSc. degree from Tabriz University Chemical Engineering Department in2016.

She completed her MSc. thesis which was “Treatment of Lignocellulosic Biomass by Co-Solvent for High Yield of Saccharification: Investigation of Structural Changes in Biomass Using FTIR Analysis” under supervision of Prof. Dr. Levent Ballice at Ege University in 2022.